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## 1. Acid Types.

Although many acid compounds are available to the oil industry, only the following types have been proven economically effective in oil well stimulation:

Inorganic Acids (Strong).

- Hydrochloric Acid (HCl).
- Hydrofluoric Acid (HCl:HF).

Other inorganic acids include Sulphamic, Sulphuric and Nitric acids.

Organic Acids (Weak).

- Acetic Acid and Glacial Acetic Acid.
- Acetic Anhydride.
- Citric Acid.
- Formic Acid.

### 1.1 Inorganic Acids.

#### 1.1.1 Hydrochloric Acid (HCl).

Hydrochloric acid is an inorganic acid and is the most commonly used acid in oil well stimulation. Hydrochloric acid has many advantages in its application as follows:

- Low cost and availability.
- Easily inhibited to prevent attack on oil-field tubulars.
- Surface tension can be controlled to aid in :
  - Penetration.
  - Wetting properties.
  - Exhibit detergency.
  - Reducing friction pressure.
- Can be emulsified for slower reaction rate.
- Exhibit de-emulsification properties for rapid clean up.
- Most reaction products are water soluble and easily removed.
- Additives to minimise or eliminate insoluble reaction products can be applied.

It has long been recognised that hydrochloric acid is the best field acid for most applications. It is however, not without limitations. Hydrochloric acid is quite reactive; therefore, it will spend quite rapidly on some formations. It is essential with hydrochloric acid to size acid treatments and pump rates to optimise this property.

The reaction rate also dictates the selection of additives that will perform their functions during the relatively short spending time. These same additives must survive the spending process and function in the spent acid. Certain materials are soluble in hydrochloric acid but not necessarily in the spent acid water. For example, calcium sulphate can be partially solubilised by hydrochloric acid, but will crystallise out as scale when the acid spends. Iron oxide will dissolve in hydrochloric acid but will re-precipitate, as the acid spends, at about a pH of 2.0. These properties require the selection of additives that will circumvent these problems.

Hydrochloric acid is normally pumped in concentrations ranging from 3.0% to 28%. The low concentration acids are used for the removal of salt plugs and emulsions. The high concentration acids are selected to achieve longer reaction times and to create larger flow channels. By far the most frequently used strength is 15%, for the following reasons :

- Less cost per unit volume than stronger acids.
- Less costly to inhibit.
- Less hazardous to handle.
- Will retain larger quantities of dissolved salts in solution after spending.

In addition to the above advantages 15% hydrochloric acid will also provide other specific properties such as emulsion control and silt suspension. The general uses for hydrochloric acid are as follows :

- Carbonate acidizing - Fracture and Matrix.
- Sandstone acidizing - Matrix only.
- Preflush for HCl:HF mixtures.
- Post-flush for HCl:HF mixtures.
- Acidizing sandstones with 15% to 20% carbonate content.
- Clean-up of acid-soluble scales.
- Perforation washes.

Pure hydrochloric acid (muriatic acid) is a colourless liquid, but takes on a yellowish hue when contaminated by iron, chlorine, or organic substances. It is available commercially in strengths up to 23.5° Bé (Baumé scale) or 38.7% percent by weight of solution.

Some processes dictate that hydrochloric acid is not the most suitable acid to use. In these cases, alternatives, such as organic acids (acetic and formic) may be used. These acids are used because of their inherently retarded nature, their ability to be used at higher temperatures and their solvation ability in "dirty" formations. The primary objection to the use of organic acids is their cost and their lack of effectiveness in removing limestone (Table 1).

**Table 1: Reaction of Acids on Limestone at Various Concentrations.**

| Acid | Concentration % | Calcium Carbonate Dissolved Pounds Per Gallon. | Carbon Dioxide Formed Cu.ft. Per Gallon. | Calcium Salt Formed Pounds Per Gallon. |
|---|---|---|---|---|
| Hydrochloric * | 15*<br>20<br>25 | 1.84<br>2.50<br>3.22 | 6.99<br>9.47<br>12.20 | 2.04<br>2.75<br>3.57 |
| Acetic | 15*<br>20<br>25 | 1.08<br>1.43<br>1.80 | 4.09<br>5.41<br>6.82 | 1.71<br>2.25<br>2.84 |
| Formic | 15*<br>20<br>25 | 1.42<br>1.90<br>2.40 | 5.38<br>7.20<br>9.09 | 1.84<br>2.47<br>3.12 |

* The most commonly used strength for hydrochloric acid is 15%, and 10% for formic and acetic acid. In this table however, HCl reaction with limestone is compared with equivalent strength formic and acetic acids, rather than to the latters commonly used strengths.

Other acids are also used in limited quantities. An example is citric acid, which can be used both alone, or as a component of an acid blend, or for use as a stabiliser, buffer and iron control agent. Also sulfamic acid has been used in the oil industry on a "do it yourself" basis. Its usage is recommended because of its low corrosivity, although it is limited by its ability to strip chrome from chrome pumps and by its relatively high cost.

### 1.1.2 Hydrofluoric Acid (HF).

Hydrofluoric acid, another inorganic acid, is used with hydrochloric acid to intensify the reaction rate of the total system and to solubilise formations, in particular sandstones. In general hydrofluoric acid is used as follows :

- It is always pumped as an HCl:HF mixture.
- Ensure that salt ion contact is prevented.
- Sandstone matrix acidizing.

- Removal of HCl insoluble fines.
- Normal concentrations 1.5% to 6.0%.
- One gallon of 12:3 HCl:HF will dissolve 0.217 pounds of sand.

Hydrofluoric occurs as a liquid either in the anhydrous form (where it is fuming and corrosive), or in an aqueous solution (as used in well stimulation). Hydrofluoric acid attacks silica and silicates, (glass and concrete). It will also attack natural rubber, leather, certain metals such a cast iron and many organic materials.

In well stimulation, hydrofluoric acid is normally used in combination with hydrochloric acid. Mixtures of the two acids may be prepared by diluting mixtures of the concentrated acids with water, or by adding fluoride salts (e.g. ammonium bifluoride) to the hydrochloric acid. The fluoride salts release hydrofluoric acid when dissolved in hydrochloric acid.

Hydrofluoric acid is poisonous, alone or in mixtures with hydrochloric acid, and should be handled with extreme caution.

### 1.1.3 Other Inorganic Acids.

Some consideration has been given to using sulfuric and nitric acids; however, these acids are not used extensively in the oil industry today. The reasons for the lack of use are; sulfuric acid will form insoluble precipitates, and nitric acid often forms poisonous gases during its reaction with certain minerals.

## 1.2 Organic Acids.

These acids are used in well stimulation basically because they have a lower corrosion rate and are easier to inhibit at high temperatures than hydrochloric acid. Although mixtures of organic acids are considered corrosive to most metals, the corrosion rate is far lower than that of hydrochloric or hydrofluoric acid, therefore, organic acids are used when long acid-pipe contact time is required. An example of this is when organic acid is used as a displacing fluid for a cement job. The organic acids is left in the production string. and is subsequently used as the perforating fluid.

Organic acids are also used when metal surfaces of aluminium, magnesium, and chrome are to be contacted, such as in trying to remove acid-soluble scales in wells with downhole pumps in place. They can also be used as iron control agents for other acid systems. Many organic acids are available, but the four most commonly used are :

- Acetic Acid.
- Acetic Anhydride.
- Citric Acid.
- Formic Acid.

### 1.2.1 Acetic Acid ($CH_3COOH$).

Acetic acid is a colourless organic acid soluble in water in any proportion and in most organic solvents. Although mixtures of acetic acid with water are considered corrosive to most metals, the corrosion rate is far lower than that of hydrochloric and hydrofluoric acids. Acetic acid is easy to inhibit against corrosion and is used frequently as a perforating fluid where prolonged contact times are required. With this ability, the acid is sometimes used as a displacing fluid on a well cementing job, where the contact time may be hours or days before perforating takes place. This ability is beneficial in three ways:

- Reduces formation damage. The first fluid two enter the formation will be an acid or low pH fluid which will react with carbonate or the calcareous materials of a sandstone formation.
- Reduces clay swelling.
- Can be used where aluminium, magnesium or chrome surfaces must be protected.

The relation of dissolving power of one gallon of a 15% concentration of acetic acid compared to that of hydrochloric acid and formic acid at the same volume is listed in

Table **1**, page 3. The cost of acetic acid per unit, based on dissolving power, is more expensive than either hydrochloric acid or formic acid.

Normally, acetic acid is used in small quantities or with hydrochloric acid, as a delayed reaction, or retarded acid. The general uses and properties of acetic acid are as follows:

- Acetic acid is relatively weak.
- Normal concentrations of 7.5% to 10% when used alone.
- Mainly used in hydrochloric acid mixtures.
- Used as an iron control additive.
- Carbonate acidizing.
- Perforating fluid.
- Retarded acids.

Commercially available acetic acid is approximately 99% "pure". It is called glacial acetic acid because, ice-like crystals will form in it at temperatures of approximately 60° F (16° C) and will solidify at approximately 48° F (9° C). When glacial acetic acid is mixed with water, a contraction occurs. For this reason, the amount of acetic acid and the amount of water normally total more than the required volume.

Care should be exercised when handling acetic acid. This solution in concentrated form can cause severe burns and fume inhalation can harm lung tissue.

### 1.2.2 Acetic Anhydride Acid.

Acetic anhydride is the cold weather version, for use instead of acetic acid due to its lower freezing point of 2.0° F (-17° C). The properties of acetic anhydride are the same for those of acetic acid, the only changes are those in relation to volumes used.

A comparison of acetic anhydride to acetic acid shows that one gallon of acetic anhydride mixed with 0.113 gallons of water is equivalent to 1.127 gallons of acetic acid. Expressed alternatively one gallon of acetic acid is equivalent to 0.887 gallons of acetic anhydride mixed with 0.101 gallons of water.

When mixing acetic anhydride always add it to water or dilute acid. If water or dilute acid is added to acetic anhydride, an explosion will occur due to a rapid increase in temperature caused by the chemical reaction.

As with acetic acid, care should be exercised when handling acetic anhydride as this solution in concentrated form can cause severe burns and fume inhalation can harm lung tissue.

### 1.2.3 Citric Acid ($C_6H_8O_7$).

Iron scales are normally found in the casing and tubing in wells and sometimes as the mineral deposits in the formation rock itself. When hydrochloric acid solutions come into contact with these scales or deposits, the iron compounds are partially dissolved and are carried in solution as iron chloride. As the acid becomes spent, the pH rises above 2.0, allowing the iron chloride to undergo chemical changes and re-precipitate as insoluble iron hydroxide. This re-precipitation can reduce formation permeability and injectivity.

Citric acid (Ferrotrol 300) is a white granular organic acid material. It is used to "tie up" dissolved iron scales and prevent re-precipitation of dissolved iron from spent hydrochloric acid solutions. Normally, citric acid (often referred to as a sequestrant or sequestering agent), is used with X-14 to make the effects of suspension more stable.

Citric acid is not used alone as an acid treating solution itself but is used in hydrochloric acid solutions known as sequestering acids (SA-systems) for the control of iron.

The amount of citric acid added to the hydrochloric acid system depends upon the amount of iron that is present. The first 50 pounds of citric acid added to 1000 gallons of acid, will sustain 2000 parts per million (ppm) of iron in solution (SA-2). Each additional 50 pounds of citric acid added will increase its sequestering property by an additional 2000 ppm, as shown in Table 2.

Iron re-precipitation depends upon the retention time of the acid in the formation and the pH of the spent acid solution. In dolomite and limestone formations, hydrochloric acid solutions can spend rapidly and as the pH reaches 2.0, the dissolved iron starts to re-precipitate. Therefore it is important to start production or swabbing operations within an hour after the acid job is complete.

The procedure for mixing sequestering acid is as follows:

1. Place dilution water in the tank.
2. Add the citric acid and X-14 whilst agitating.
3. Blend until dissolved.
4. Add the inhibitor, surfactants, and finally add the raw hydrochloric acid.

In sandstone formations, if the acid solubility is low, the pH of the spent acid may stay below a pH of 2.0, and iron sequestering agents may not be needed.

**Table 2: Control of Iron with Citric Acid.**

| Acid System | Iron Concentration Control, ppm. |
|---|---|
| SA-2 | 2,000 |
| SA-4 | 4,000 |
| SA-6 | 6,000 |
| SA-8 | 8,000 |
| SA-10 | 10,000 |

### 1.2.4 Formic Acid (HCOOH).

Formic acid is the simplest of the organic acids and is completely miscible (capable of being mixed) with water. Formic acid is stronger than acetic acid yet weaker than hydrochloric acid. Formic acid is used in well stimulation, most frequently in combination with hydrochloric acid as a retarded acid system for high-temperature wells. The percentage of formic acid used in such applications is commonly between 8.0% and 10%. Formic acid can be easily inhibited, but not as effectively as with acetic acid at high temperatures and long contact times. The properties and uses of formic acid parallel those of acetic acid as stated below:

- Formic acid is relatively weak.
- Seldom used alone.
- Mainly used in hydrochloric acid mixtures.

- Corrosion inhibitor aid.
- Hot wells.
- Retarded acids.

Acetic acid, acetic anhydride and formic acid are used when exceptionally retarded acid is needed because of extreme temperature or very low injection rates. At high temperatures, blends of organic and hydrochloric acid are much more successfully inhibited by organic inhibitors, than when hydrochloric acid is used alone. This property minimises the danger of hydrogen embrittlement of steel associated with hydrochloric acid treatments in high-temperature wells. Organic acid concentrations of up to 25% by weight are required, making acid treatment costs increase. Organic acids do not give as much reacting capability as hydrochloric acid treatments (see

Table **1**, page 3).

BJ Services Super Sol (EQH) acid systems give equivalent reacting capacity of regular hydrochloric acid strengths. The Super Sol acid systems have improved corrosion inhibition and longer reaction times. These properties allow more effective treatment of hot carbonate reservoirs with stronger acids. The Super Sol acid systems are a mixture of hydrochloric acid and an organic acid having the same limestone reacting capacity as an equal volume of 10%, 20% or 30% hydrochloric acid.

## 2. Acid Chemistry.

### 2.1 General Chemistry.

#### 2.1.1 Acids.

An acid is a compound that when dissolved in (or hydrolysed by) water, it releases hydrogen ions ($H^+$) as the cation. Examples of commonly used acids are as follows :

| | | | | | |
|---|---|---|---|---|---|
| Hydrochloric Acid. | $HCl + H_2O$ | $\rightarrow$ | $H^+$ | + | $Cl^-$ |
| Hydrofluoric Acid. | $HF + H_2O$ | $\rightarrow$ | $H^+$ | + | $F^-$ |
| Acetic Acid. | $H_3C\text{-}COOH + H_2O$ | $\rightarrow$ | $H^+$ | + | $H_3C\text{-}COO^-$ |
| Formic Acid. | $HCOOH + H_2O$ | $\rightarrow$ | $H^+$ | + | $HCOO^-$ |
| Sulfamic Acid. | $H_2N\text{-}SO_2OH + H_2O$ | $\rightarrow$ | $H^+$ | + | $H_2N\text{-}SO_3^-$ |
| Water. | $HOH + H_2O$ | $\rightarrow$ | $H^+$ | + | $OH^-$ |

#### 2.1.2 Bases.

A base is a compound that when dissolved in (or hydrolysed by) water, produces hydroxyl ions ($OH^-$) as the anion. Some examples of common bases are as follows :

| | | | | | |
|---|---|---|---|---|---|
| Sodium Hydroxide. | $NaOH + H_2O$ | $\rightarrow$ | $OH^-$ | + | $Na^+$ |
| Potassium Hydroxide. | $KOH + H_2O$ | $\rightarrow$ | $OH^-$ | + | $K^+$ |
| Calcium Hydroxide. | $Ca(OH)_2 + H_2O$ | $\rightarrow$ | $2OH^-$ | + | $Ca_2^+$ |
| Ammonia Gas. | $NH_3 + H_2O$ | $\rightarrow$ | $OH^-$ | + | $NH_4^+$ |

#### 2.1.3 Salts.

A salts is a compound formed by the reaction of an acid with a base. The reaction is usually quite rapid and liberates a large quantity of heat. Some common examples of salt formation are :

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| Sodium Chloride | $HCl + NaOH$ | $\rightarrow$ | $NaCl$ | + | $H_2O$ | | |
| Calcium Chloride | $2HCl + CaCO_3$ | $\rightarrow$ | $CaCl_2$ | + | $CO_2\uparrow$ | + | $H_2O$ |
| Silicon Tetrafluoride | $4HF + SiO_2$ | $\rightarrow$ | $SiF_4$ | + | $2H_2O$ | | |
| Barium Sulphate | $H_2SO_4 + Ba(OH)_2$ | $\rightarrow$ | $BaSO_4$ | + | $2H_2O$ | | |
| Magnesium Formate | $2HCOOH + Mg(OH)_2$ | $\rightarrow$ | $Mg(HCOO)_2$ | + | $2H_2O$ | | |

### 2.2 Reactions of Hydrochloric Acid (HCl).

| | | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| Hydrochloric Acid | + | Calcium Carbonate | → | Calcium Chloride | + | Carbon Dioxide | + | Water |
| $2HCl$ | + | $CaCO_3$ | → | $CaCl_2$ | + | $CO_2\uparrow$ | + | $H_2O$ |
| Hydrochloric Acid | + | Dolomite | → | Calcium Chloride | + Magnesium Chloride | + Carbon Dioxide | + | Water |
| $4HCl$ | + | $CaMg(CO_3)_2$ | → | $CaCl_2$ | + $MgCl_2$ | + $2CO_2\uparrow$ | + | $2H_2O$ |
| Hydrochloric Acid | + | Sand | → | No appreciable reaction. | | | | |
| $HCl$ | + | $SiO_2$ | → | No appreciable reaction | | | | |

## 2.3 Reactions of Hydrofluoric Acid (HF).

| | | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| Hydrofluoric Acid | + | Calcium Carbonate | → | Calcium Bifluoride | + | Carbon Dioxide | + | Water |
| $HF$ | + | $CaCO_3$ | → | $CaF_2$ | + | $CO_2\uparrow$ | + | $H_2O$ |
| Hydrofluoric Acid | + | Sand | → | Fluosilicic Acid | + | Water | | |
| $6HF$ | + | $SiO_2$ | → | $H_2SiF_6$ | + | $2H_2O$ | | |
| Fluosilicic Acid | + | Sodium | → | Sodium Fluosilicate | + | Hydrogen | | |
| $H_2SiF_6$ | + | $2Na$ | → | $Na_2SiF_6$ | + | $H_2\uparrow$ | | |
| Hydrofluoric Acid | + | Bentonite Clay | → | Fluosilicic Acid | + | Fluoaluminic Acid | + | Water |
| $36HF$ | + | $Al_2(Si_4O_{10})(OH)_2$ | → | $4H_2SiF_6$ | + | $2H_3AlF$ | + | $2H_2O$ |

## 2.4 Reactions of Acetic Acid.

| | | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| Acetic Acid | + | Calcium Carbonate | → | Calcium Acetate | + | Carbon dioxide | + | Water |
| $2HCH_3CO_2$ | + | $CaCO_3$ | → | $Ca(CH_3CO_2)_2$ | + | $CO_2\uparrow$ | + | $H_2O$ |

## 2.5 Reactions of Formic Acid.

| | | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| Formic Acid | + | Calcium Carbonate | → | Calcium Formate | + Carbon dioxide | + Water | | |
| $2HCCO_2H$ | + | $CaCO_3$ | → | $Ca(HCO_2)_2$ | + $CO_2\uparrow$ | + | | $H_2O$ |

## 3. Acidizing Limestones, Dolomite and Sandstone Formations.

Much of the worlds oil and gas comes from limestone ($CaCO_3$) and dolomite ($CaMg(CO_3)_2$) formations, either in their relatively pure form or in the form of carbonate or siliceous sands cemented together with calcareous materials ($CaCO_3$). Dolomites are similar to limestones with the exception that they generally react more slowly with hydrochloric acid.

The primary method of stimulating wells drilled into these formations is to inject an acid treating solution. The acid dissolves part of the formation and may also dissolve other acid soluble material (mud damage, scales etc.), which is restricting or blocking the flow of oil or gas from the formation. Matrix acidizing increases the flow capacity of a producing formation when these restrictions are removed.

### 3.1 Limestone and Dolomite.

When either limestone and/or dolomite formation are stimulated, acid enters the formation through pores in the matrix of the rock or through natural or induced fractures. The type of acidizing used depends on, the injection rate and the number and size of the fractures present. Most limestone and dolomite formations produce through a network of fractures, though both formations can exist in an unfractured state. Normally, an interval will accept acid through the fractures more readily and at lower pressure than through the pore spaces. The acid solution reacts with the walls of the flow channels, increasing the width and conductivity of the fractures.

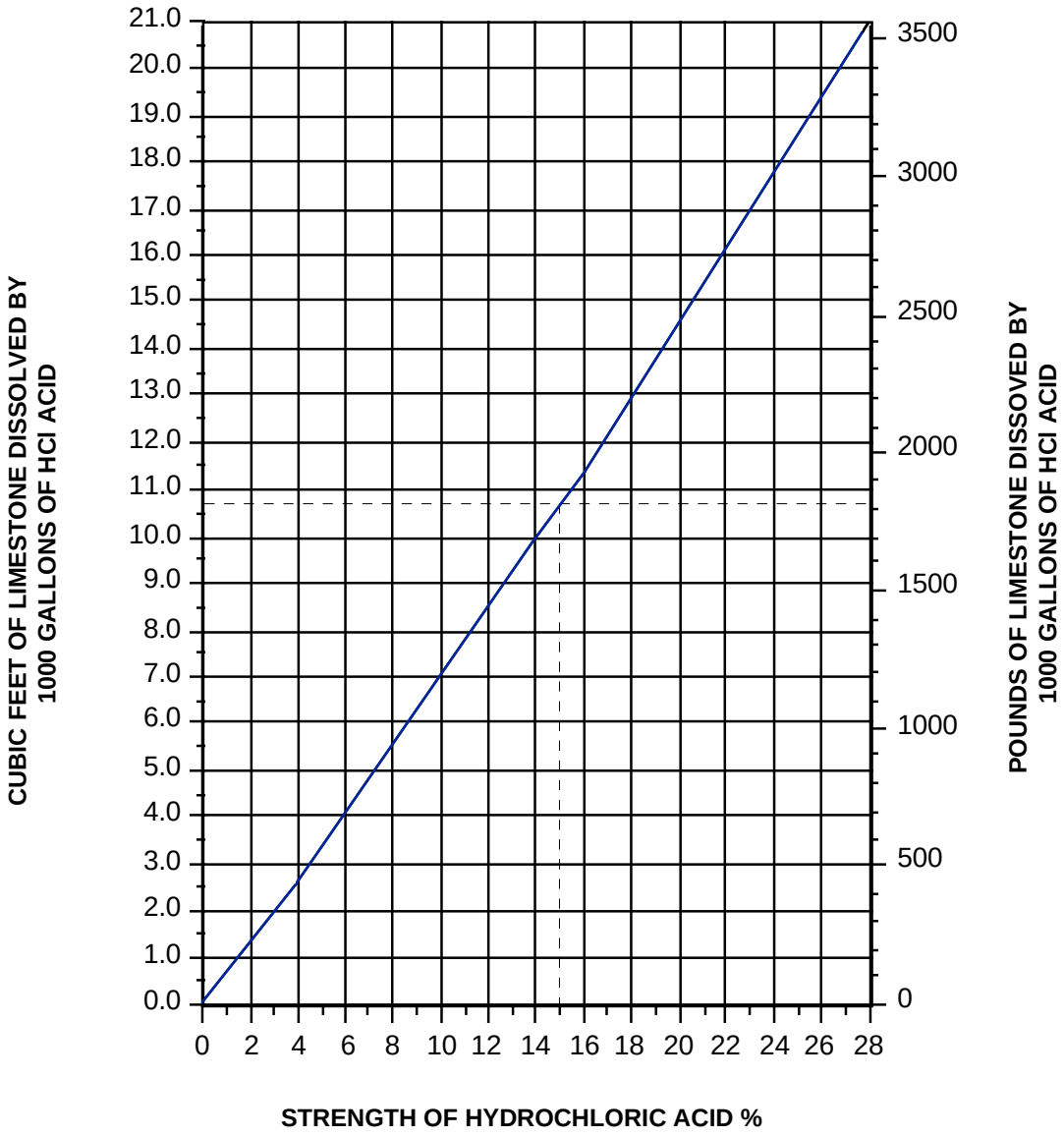
Most limestones and dolomite formations vary in acid solubility. Acid will attack the surface of the formation at varying rates, leaving an unevenly etched face. The existence of natural fractures, that occur at random intervals and in random sizes, contribute to the final uneven etching configuration.

The type of acid and strength are equally important factors in influencing the etch pattern. The amount of limestone dissolved by 1000 gallons hydrochloric acid at different strengths is shown in Figure 1. The use of various types of acid (such as chemically retarded or emulsified acid), ensure that the volume of limestone or dolomite dissolved, will occur in an uneven pattern across the face of the fracture. Gelled and cross-linked acids can also be used effectively. These fluids will create wider fractures and have reduced leak-off, resulting in less “worm holing” and deeper penetration due to the retarded reaction of the acid.

Chemically retarded acids are made effective by preceding the acid treatment with a hydrocarbon preflush containing an oil-wetting surface acting agent (surfactant) Due to the variable composition of the rock, the surfactant leaves a discontinuous oil film on the fracture face. The resulting acid break-through is irregular, creating an improved etch pattern.

With emulsified acid, the resulting etch patterns are influenced by the rate at which acid penetrates the hydrocarbon outer phase of the emulsion and reacts with the formation face.

**Figure 1: Amount of Limestone Dissolved by 1000 Gallons of Hydrochloric Acid.**




The temperature of the formation should also be considered to ensure that the selection of either chemically retarded acid or delayed reaction acid is the one that is most suitable for the treatment recommended. Desired acid strengths for different temperatures are shown in Table (page 21).

Acid volume and pump rate determine the acid contact time, during which the fracture faces are exposed to live acid. Contact time has a direct bearing on the amount of etching obtained. However, increasing the volume of an acid treatment does not appreciably increase the depth of penetration. Thus, the benefit of a

treatment with a contact time greater than the spending time of the acid, can be attributed to acid etching, which results in additional flow conductivity.
The "shut-in time", or the length of time a well is closed in after a stimulation treatment, is determined by the type of acid used and by such downhole factors as:

- Type of formation.
- Bottom-hole temperature.
- Bottom hole pressure.

After an acid solution has been neutralised by reaction with the formation, it is no longer a stimulation agent. However, it may become harmful to the formation permeability if allowed to remain downhole.

Hydrochloric acid reacts so rapidly with limestone formations that it is essentially neutralised by the time the acid has been completely placed. This neutralisation generally occurs at all ranges of temperature and pressure. Limestone formations incorporate varying amounts of insoluble impurities, which can plug permeability if allowed to come to rest. Therefore, it is important to remove the neutralised hydrochloric acid as soon as possible. The shut-in time with such formations is zero. Figures 2 to 5 show the relative reaction rates of 15% hydrochloric acid with limestone and dolomite formations at different temperatures.

When chemically retarded acids like super retarded acids (SRA), delayed reaction systems (Super Sol Acid (EQH)), Sta-Live and emulsified acids like SRA-3 are used, the reaction time exceeds the displacement time. This is also true for gelled and cross-linked acids (Gelled Acid, Gelled Acid XL, XL Acid II). Here, the shut-in time may be extended if there is sufficient bottom-hole pressure to promote rapid clean-up. For reaction times of retarded acids consult the engineering product bulletin pertaining to the acid system used.

**Figure 2: Relative Reaction Rates of 15% HCl with Limestone Formations at 75° F.**

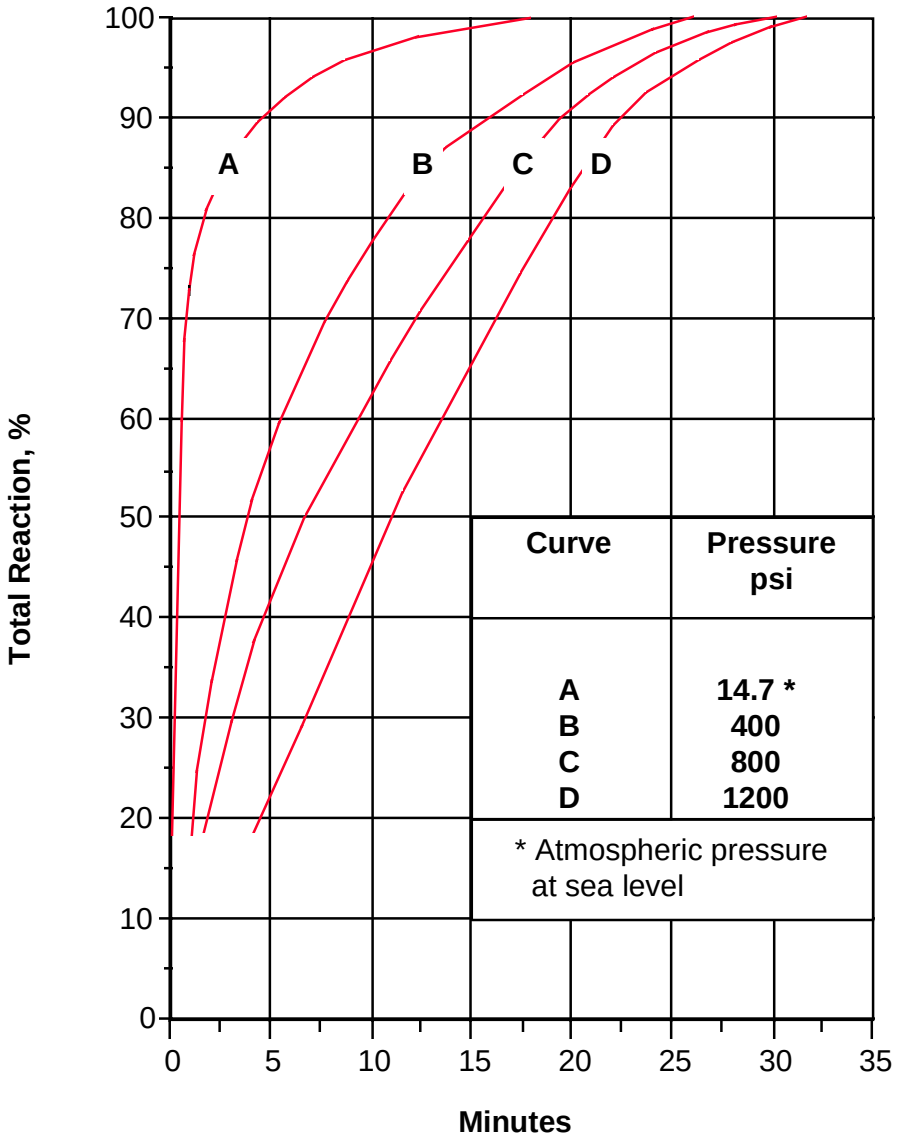


**Figure 3: Relative Reaction Rates of 15% HCl with Limestone Formations at 140° F.**

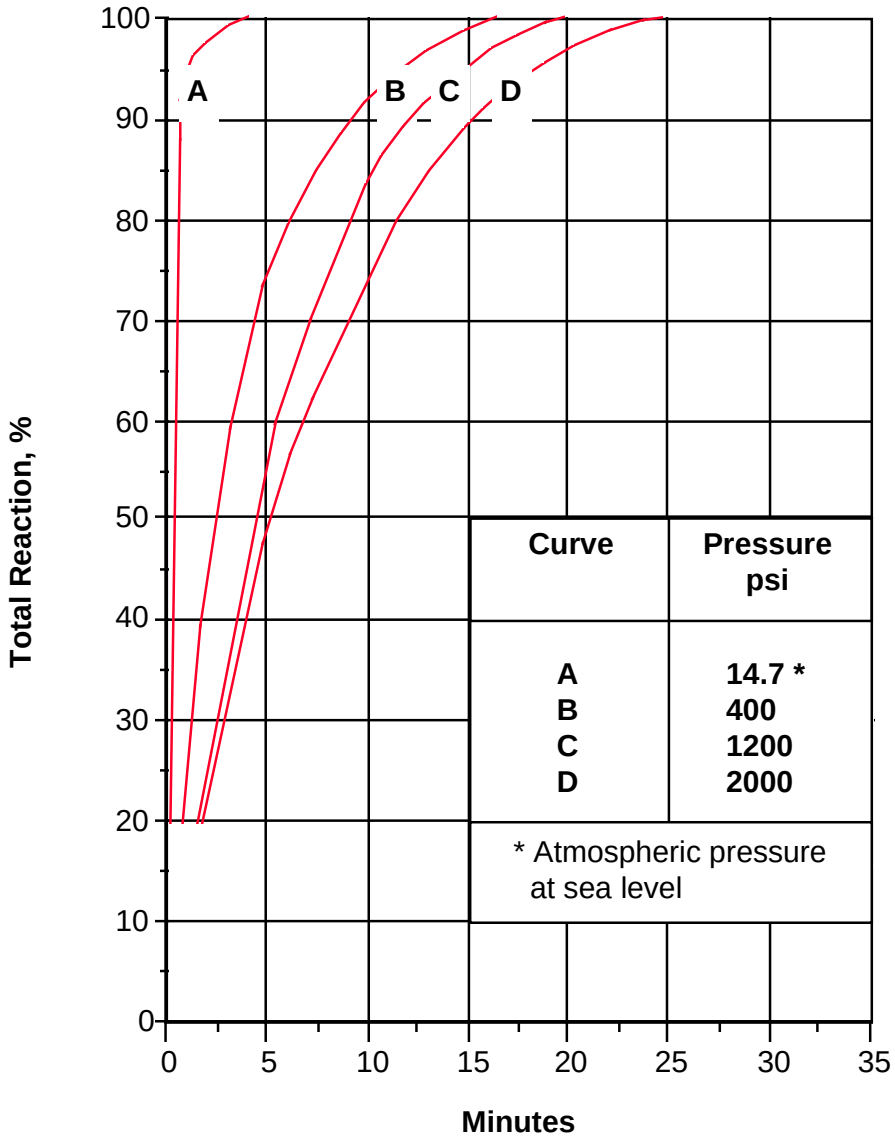


**Figure 4: Relative Reaction Rates of 15% HCl with Dolomite Formations at 75° F.**

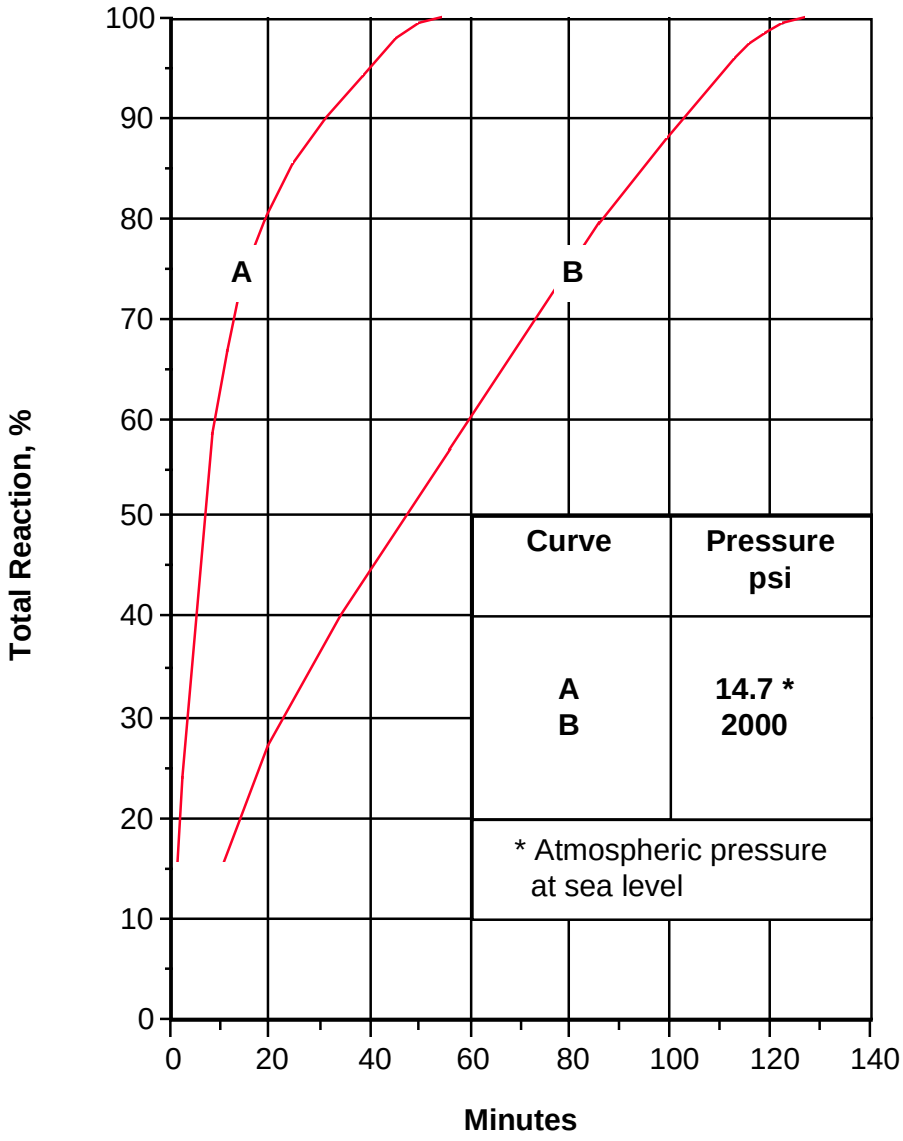
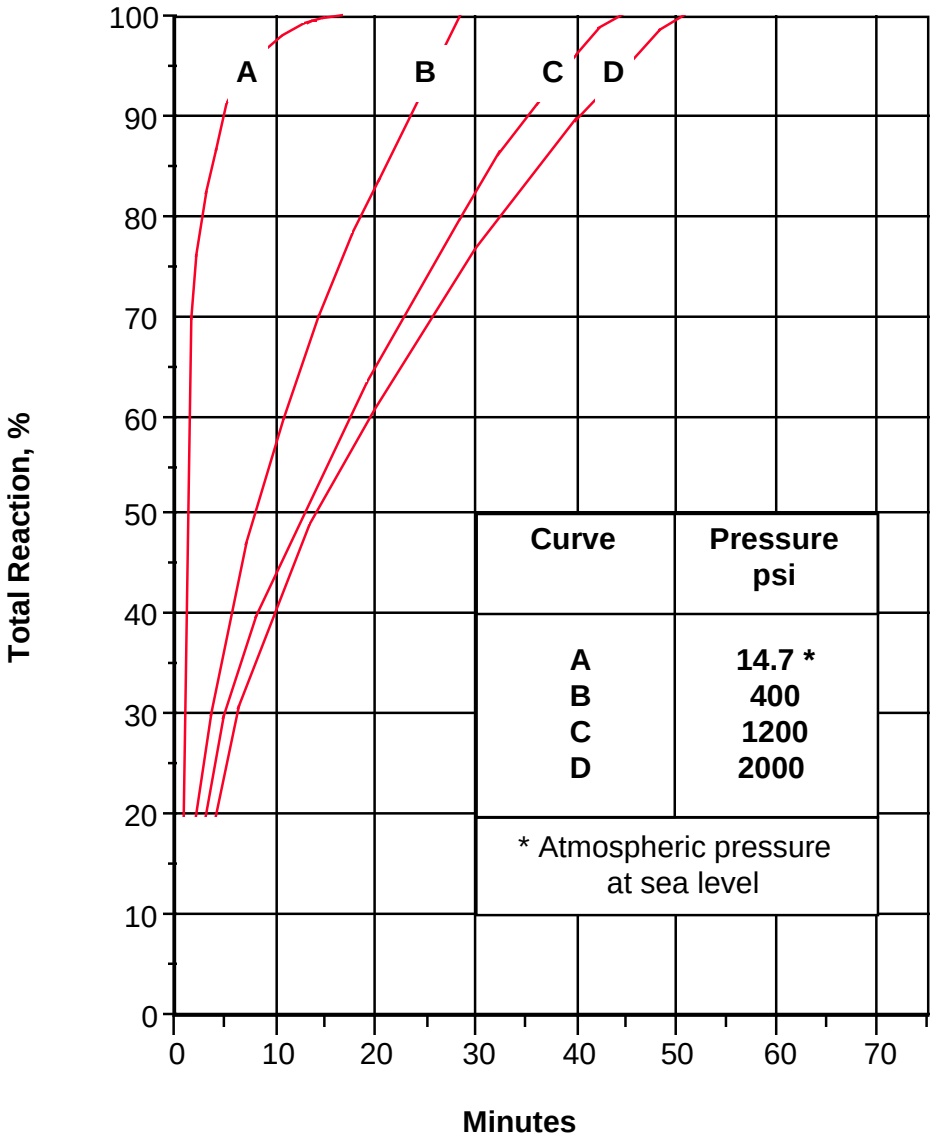


**Figure 5: Relative Reaction Rates of 15% HCl with Dolomite Formations at 140° F**



### 3.2 Sandstone Acidizing.

The primary purpose of sandstone acidizing is to stimulate the permeability of the formation. Matrix type treatments are used in most cases. Limestone and dolomite formations react at high rates with hydrochloric acid and at moderate rates with formic and acetic acids. Sandstone formations, however, react little, if at all, with these three acids.

Most sandstone formations are composed of quartz particles, silicon dioxide ($SiO_2$) bonded together by various kinds of cementing materials, chiefly carbonates, silica and clays. The amount of reaction with hydrochloric, formic and acetic acids is limited to the amount of calcareous material present in the formation. However, the silicon dioxide and the clay will react with hydrofluoric acid, even though the reaction rate is slow compared to the reaction of hydrochloric acid with limestone.

Since hydrofluoric acid reacts with sands (silica), silt, clay and most drilling muds, it has been found to be effective in stimulating, and removing formation damage from and in stimulating sandstone reservoirs. Hydrofluoric acid is normally used in combination with hydrochloric acid in mixtures which range in strength from 6.0% HCl with 0.5% HF to 28.0% HCl with 9.0% HF. The most common strength used is 12.0% HCl with 3.0% HF, and is usually referred to as Regular Mud Acid (RMA) or mud acid.

Some situations may require 15.0% HCl with 3.0% or 4.0% HF for effective sandstone stimulation. The best ratio or concentration of HCl:HF strength should be determined by laboratory core tests. HCl:HF acid strengths above the 4.0% HF concentration should be avoided because disassociation of the formation can occur. Other common HCl:HF strengths are listed below:

**Table 3 : Common Strengths of HCl:HF Mixtures.**

| % HCl | % HF |
|---|---|
| 6.0 | 0.5 |
| 7.5 | 1.5 |
| 12 | 3.0 |
| 15 | 3.0 |
| 15 | 4.0 |

Ammonium bifluoride salt is nearly always used to make up HCl:HF mixtures. It is preferred, to the use of liquid hydrofluoric acid, for two reasons :

- Liquid hydrofluoric acid is extremely hazardous to handle.
- The ammonium ions, produced in solution, act as a buffer that minimises the formation of precipitates

The hydrochloric acid in these formulations has three purposes:

- It acts as a converter to produce hydrofluoric acid from the ammonium bifluoride salt.
- It dissolves the hydrochloric acid-soluble material and thus prevents the hydrofluoric acid from spending too rapidly.
- It prevents the precipitation of Calcium Bifluoride ($CaF_2$).

The basic factors controlling the relative reaction rate of hydrofluoric acid within the matrix are; temperature, acid concentration, pressure, chemical composition of the formation rock, and the ratio of rock area to acid volume.

Temperature has a marked effect on the reaction rate of hydrofluoric acid with sand and clay. The rate of reaction approximately doubles for each 50° F (28° C) increase in temperature. **Table 4** shows the recommended maximum acid strengths for use at different temperatures.

**Table 4: Recommended Maximum Acid Strengths at Different Temperatures.**

| Temperature | Maximum HCl Strength | Maximum HCl:HF Strength |
|---|---|---|
| Up to 180° F (82° C) | 15% | 12.0:3.0% |
| 180° F to 220° F (82° C to 104 °C) | 10% | 9.0:3.0% |
| Above 220° F (104° C) | 7.5% | 7.5:1.5% |

Surprisingly, reaction rate also increases with pressure, even though most reactions that produce a gas (such as the reaction of silicates with hydrofluoric acid) are retarded by pressure. The formation of fluorosilicic acid ($H_2SiF_6$) from evolved gas, silicon tetrafluoride ($SiF_4$), contributes to the overall reaction of the formation, which could explain the increased reaction rate of hydrofluoric acid under pressure.

The rate of reaction also doubles as the concentration doubles; for example, a 12.0% : 4.0% solution of hydrofluoric acid reacts twice as fast as a 12.0% : 2.0% solution, with clays and silicates.

The relative amounts of sandstone, clay, silt and calcareous materials in any given formation also affect the reaction rate. Each material has its own characteristic reaction rate with hydrofluoric acid. For example, hydrofluoric acid reacts with clay at a faster rate than with sand, and with calcareous material at a faster rate than with clays.

### 3.2.1 Optimising HCl:HF Acid Strength from Core Flow Studies.

To optimise the strength of HCl:HF mixtures used in sandstone stimulation, tests are carried out with several hydrochloric and hydrofluoric acid mixtures. These tests are run using sandstone cores at simulated bottom hole temperatures. The hydrofluoric acid in the acid mixtures serves two essential purposes:

- Dissolves and disperses clays present in the sandstone.
- Dissolves the silica coating that covers many carbonate deposits present in the formation allowing the hydrochloric acid present to react with these deposits.

Removal of the clays can lead to large increases in the flow improvement ratio, whilst removal of the silica coating, allowing dissolution of the carbonate deposits increases formation solubility. The overall effect of these two actions is significant increases in reservoir productivity.

To simulate actual flow conditions in a reservoir, initial permeability of the core is established by flowing brine through the core sample. Acid stimulation fluids are then flowed through the core in the opposite direction. Core permeability after acidizing (return permeability) is then measured by flowing brine or other fluids in the original direction. In this way flow of fluids to and from the wellbore are simulated as they would occur in the producing formation.

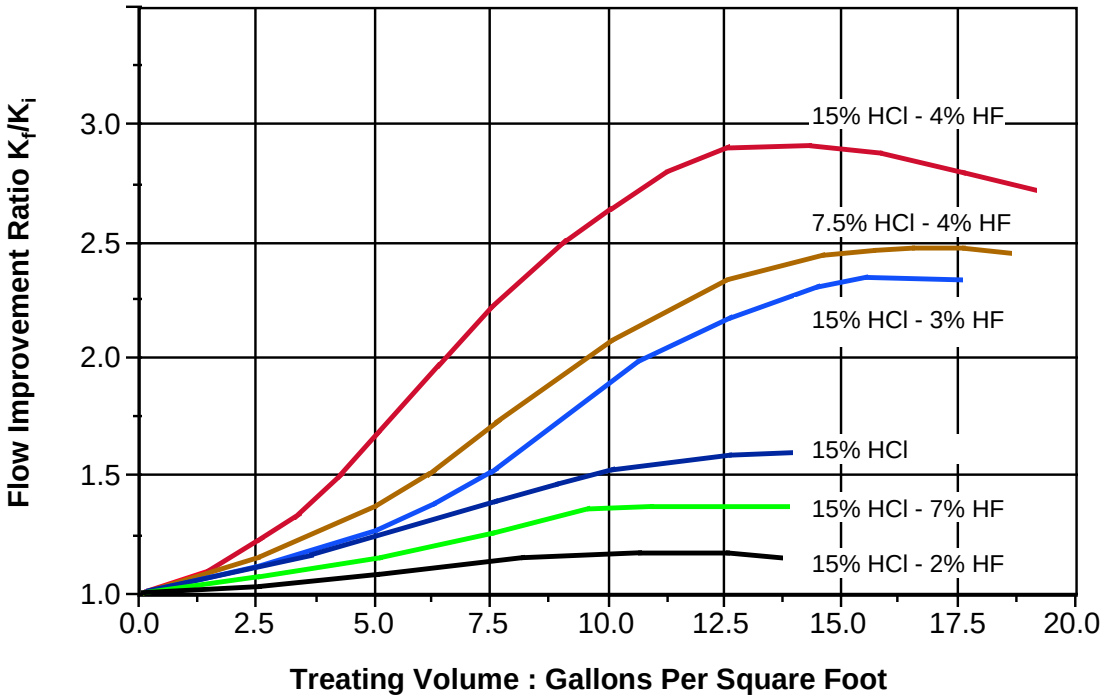
From the test results obtained, core permeability after stimulation (final permeability, $K_f$) can be compared with the initial permeability ($K_i$), and expressed as a flow improvement ratio:

$$\frac{K_f}{K_i} = \text{Flow Improvement Ratio.}$$

Figure 6 shows the effect of various HCl:HF acid concentrations on the flow improvement ratio of Berea Sandstone (a universal laboratory testing medium). Clearly the maximum flow improvement ratio was obtained with a mixture of 15.0% HCl and 4.0% HF acid.

From the data produced with Berea Sandstones, it can be seen that acid concentrations of less than 15.0% HCl and 4.0% HF are not as efficient at dissolving clay and silicates, therefore the flow improvement ratios are lower.

**Figure 6: Flow Improvement Ratio of Various Treating Solutions in Berea Sandstones.**




Hydrofluoric acid concentrations above 4.0% should not be used. As can be seen in Figure 6 above, the 15.0% HCl to 7.0% HF mixture, deteriorates the core causing a decrease in permeability.

The use of high concentrations of hydrofluoric acid cause sand formations to become unconsolidated, and can create problems by promoting the production of sand. This process is caused by the removal of too much of the silica and carbonate cementing materials present in the formation.

Generally a few pore volumes of 15.0%:7.0% mix of HCl:HF acid will unconsolidate a core, whereas many pore volumes of the 15.0%:4.0% mixture will leave the same core intact. In addition, a 15.0%:7.0% mix of hydrofluoric acid will form a large volume of precipitates. This is particularly true where the solution is made up from liquid hydrofluoric acid as opposed to ammonium bifluoride. The reason for the lesser problem with the ammonium salt is that, when the ammonium ions are dissociated and in solution they act as a chemical buffer which helps maintain a low pH thus minimising precipitation.

If representative cores are not available, the optimum volumes and concentrations should be determined by using local experience and guidelines presented in this manual, such as the Berea sandstone curves given in Figure 6. Since the ratios for a given reservoir can vary substantially, no generalised set of flow improvement ratios are presented for various formations.

### 3.2.2 Prevention of Precipitation of Reaction By-Products.

Because fluorine is a very reactive element and because the composition of sandstone is varied, many reaction products are formed when sandstone formations are stimulated with hydrofluoric acid. For example calcium bifluoride ($CaF_2$) is formed when hydrofluoric acid reacts with calcium carbonate ($CaCO_3$).

As long as live HCl:HF acid is present, the calcium fluoride (an undesirable product), remains ionised and in solution. However, in the absence of hydrofluoric or hydrochloric acid, calcium bifluoride may be precipitated. Maintaining a low pH and using a short shut-in time ensures against the deposition of calcium bifluoride. A preflush of hydrochloric acid is also used to react with and remove the calcium and magnesium carbonates in the formation.

Sodium and potassium ions that may be present in the formation water can react with hydrofluoric acid to form insoluble precipitates, such as sodium or potassium hexafluosilicate ($Na_2SiF_6$ or $K_2SiF_6$).

When this possibility exists, a preflush of hydrochloric acid should always be used ahead of the hydrofluoric acid treating solution to displace the formation water. Brines and sea water should never be used to prepare this treating fluid, as the metal ions present in solution, can react to form precipitates with hydrofluoric acid.

The use of 15% HCl as a preflush serves three purposes:

- It removes calcium and magnesium carbonates.
- It minimises the loss of the hydrofluoric acid used in the second phase of a treatment.
- It serves as a spacer between the HCl:HF acid and the formation brine.

Other preflushes and fluids which can be used to provide a barrier include:

- Ammonium Chloride (2.0% to 4.0%). Also acts as a chemical buffer to prevent formation of precipitates.
- Diesel oil.
- Kerosene.
- Clean Lease oil.

A post-flush of 3.0% to 15% HCl should be used as a pad to separate the HCl:HF acid from the displacement fluid. This post-flush will prevent the formation of precipitates, by preventing brine from mixing with the HCl:HF acid during displacement, and act to maintain a low pH as the spent acid is produced back. Sufficient volume should be used to displace the HCl:HF acid out into the formation and reduce the risk of damage from precipitation in the near wellbore area. Other post-flushes include:

- Ammonium Chloride (2.0% to 4.0%). Also acts as a chemical buffer to prevent formation of precipitates.
- Diesel oil.
- Kerosene.
- Clean Lease oil.

Shut in times should be kept to a minimum to reduce the possibility of precipitation of reaction by-products that might reduce the effectiveness of the stimulation treatment.

## 4. Acid Treatments.

Acid treatments are applied by one of three techniques:

- Soaking-Agitation.
- Fracture Acidizing.
- Matrix Acidizing.

### 4.1 Soaking-Agitation (Perforation Cleaning).

The number of soaking and agitation applications depends upon the amount of damage that has occurred in the perforations or in the immediate area of the wellbore. Acid solutions designed for suspension, solvent acid dispersions, or clean-up types are normally used in soaking action. This soaking action allows the acid to work on the acid-soluble materials and remove mud filtrate, silts and other debris that might plug the formation. Agitation can be accomplished by one of three methods:

1. The acid can be spotted across the perforations to allow a short soaking period and then washed back through the annulus whilst the work-string is moved up and down through the zone of interest.

2. Pressure is applied against the perforations without exceeding the bottom hole fracturing pressure (BHFP) and then releasing this pressure very quickly through the bleed off at the pumping unit. This action is sometimes referred to as "back-surging".

3. Acid is spotted across the perforations and allowed to soak for a few minutes, then it is "swabbed back" either through the tubing or casing.

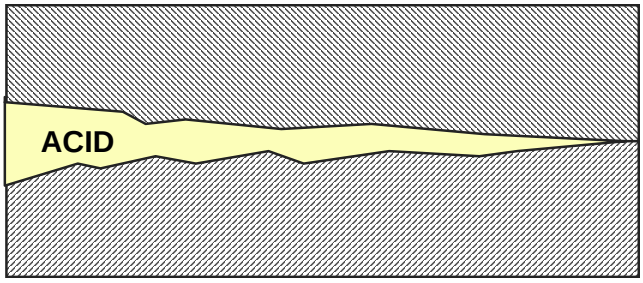
With any of the above methods, acid may have to be applied several times before the formation is opened for fluid entry. The use of several applications allows a regular acid job to be performed without fear of pushing unwanted plugging material into the natural permeability or flow channels of the formation.

Non-acid chemical treatments are used to treat for scale deposits, water blocks, bacteria, clay damage, or water shut-off systems. These types of treatment are applied either by injecting into the formation or by soaking for a prescribed time (up to 24 hours).

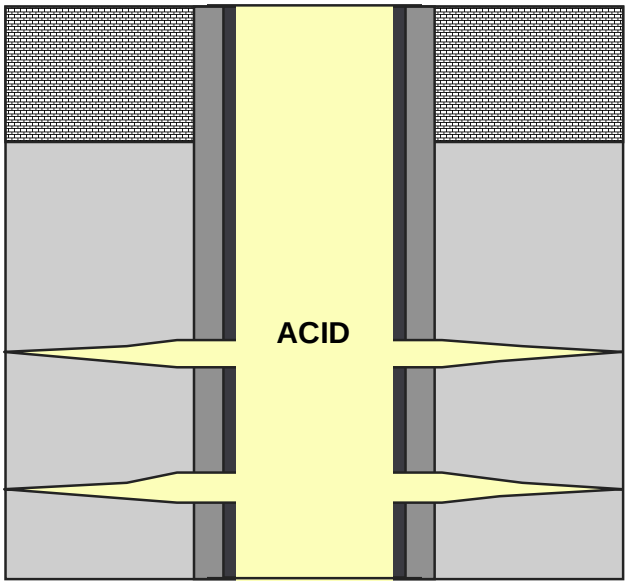
## 4.2 Fracture Acidizing (Limestones and Dolomites).

In fracture acidizing, the acid is injected through natural or induced fractures at pressures usually exceeding the formation's fracture pressure (Figure 7). This type of stimulation enlarges or creates flow channels from the formation to the wellbore, thus increasing the flow of oil or gas. In fracture acidizing, acid penetration depends upon the velocity of the acid, its reaction rate with the formation, the contact area between the fractures and the acid, and the leak-off rate of the acid.

**Figure 7: Fracture Acidizing.**




(a) Fracture acidizing involves the injection of acid down the well at a rate faster than the formation can accept it by way of the natural flow channels.




(b) Since the rock will not accept all of the acid, pressure builds up. Finally the rock ruptures and the acid is injected down a fracture within the limestone formation.

Most experts agree that the maximum penetration of acid is achieved when the first increment of injected acid is completely neutralised. Whilst later increments of live

acid accomplish additional etching of the fracture faces, they do not penetrate any greater distance from the wellbore than did the first increment.
This etching creates an uneven fracture face which helps prevent the fractures from completely closing when the pressure is released. An additional benefit to the production of oil and gas is a zone of increased matrix permeability adjacent to the fracture faces created by the leak-off of live acid into the formation. This increased permeability can help improve well productivity even where almost total closure of the fracture occurs.

Velocity of the acid in a given naturally fractured formation is determined primarily by the injection rate. The deepest penetration can be obtained from a rate that will produce an injection pressure just slightly below the pressure required to create additional fractures. Any pressure greater than this optimum will widen existing fractures and open up new ones, thus decreasing the fluid velocity.

The reaction rate of the acid probably has the greatest effect on the depth of penetration with this method. BJ Services has developed several acid systems such as Gelled Acid, Cross-linked acid (XL Acid) and Emulsified Acid (SRA-3) to retard the reaction rate of hydrochloric acid with limestone and dolomite formations for deeper penetration of live acid.

An alternative method of fracture acidizing limestone and dolomite is to pump the treating solution at high rates and pressures to hydraulically fracture the formation, thus achieving deep penetration of the live acid.

Since acid itself is not an efficient fracturing fluid, due to its inherently low viscosity and high reaction rate, the use of a fluid loss additives will help to confine the acid to the flow channels by reducing leak-off. This results in deeper penetration of the formation with a given volume of treating solution. In addition water or brine with the proper gelling agents and fluid loss additives may be used as a spearhead to create the fractures. The trailing acid then enters the formation and reacts with the walls of the induced fractures. Alternatively, Cross-linked Acids can be used as the spearhead or main treatment for this purpose.

To obtain the maximum flow capacity with this technique, the acid must etch an uneven pattern on the fracture faces. The fractures tend to heal after treatment, but the creation of an uneven etching pattern can maintain communication between the wellbore and the deep fractures.

Again, leak-off of acid to the formation adjacent to the fracture faces will create a zone of increased permeability aiding this process. Three factors that influence the type and amount of etching in the fracture are:

- Rock properties.
- Type of acid.
- Contact Time.

### 4.2.1 Rock Properties.

In fracture acidizing the acid reacts with the faces of the fracture to produce an irregular etch pattern. Most limestone and dolomite formations vary in acid solubility even within the formation. Acid will attack such formations at varying rates, leaving an unevenly etched face. Zones of more variable composition and acid solubility will show a better, more irregular etch pattern than formations with homogeneous composition. Another factor is naturally existing fractures. These occur at random intervals and in random sizes contributing to the final uneven etching configuration.

### 4.2.2 Type of Acid.

This is an equally important factor. Chemically retarded acids are made effective by preceding them with a hydrocarbon preflush containing an oil-wetting surfactant. Due to the variable rock composition, the surfactant leaves a discontinuous oil film on the fracture face. The resulting acid break-through is irregular, creating an irregular etch pattern.

Emulsified acids are also used. Here the resulting etch patterns are influenced by the rate at which acid penetrates the hydrocarbon outer phase of the emulsion and reacts with formation face.

Gelled and Cross-linked Acid systems help provide leak-off control and fracture extension during the job. The viscosity provides some retardation which helps place live acid deeper into the fracture. These systems also have excellent insoluble fines suspending properties. The fines are returned to the wellbore, carried by the residual viscosity of the spent acid. A final advantage of these fluids is their ability to produce stable, high viscosity foams for use in acid foam fracs.

### 4.2.3 Contact Time.

The pumping rate and the total volume of acid pumped determine the contact time of live acid with the fracture faces. Contact time has a direct bearing on the amount of etching obtained. Depth of penetration is not increased appreciably by increasing the volume of the treatment, as there seems to be an optimum volume above which, large amounts of acid may smooth out any irregularities in the etch pattern.

Any additional benefits seen from a treatment having a contact time greater than the spending time of the acid, can be attributed to the additional flow conductivity that results from acid etching and increased permeability adjacent to the fracture faces caused by leak-off of the live acid.

### 4.2.4 Spearhead Acid Control Technique.

When designing acid fracturing treatments, determination of the volume required for effective acid penetration to a specific depth is difficult to achieve. Acid reaction rates in the fracture cannot be accurately predicted, and the true acid leak-off rate to the formation from the fracture face is difficult to determine.

By using Spearhead Acid Control (SAC) techniques these problems can be minimised. With this technique a non-acidic, high viscosity, low fluid loss, aqueous spearhead, is pumped ahead of the acid. This fluid creates the fracture and places a temporary protective film over the fracture faces. This film restricts fluid leak-off and under certain conditions, delays the reaction of the acid with the formation during placement into the fracture system.

Shortly after placement, the acid disperses the protective film, allowing leak-off and acid reaction with the formation to occur. When this reaction is complete, the "pillaring" effect resulting from the uneven solubility of the formation leaves long fractures of high conductivity.

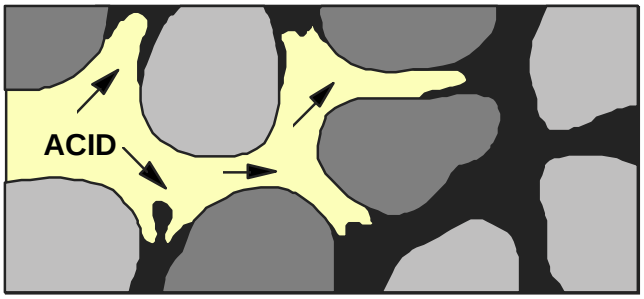
Since the leak-off and reaction time of the acid are effectively controlled, the acid can be considered as a normal fracturing fluid for the purposes of calculations when designing the job.

## 4.3 Matrix Acidizing.

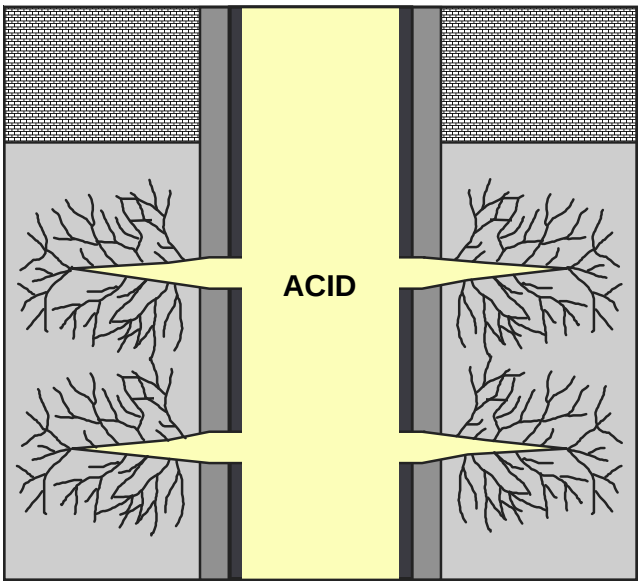
In matrix acidizing, acid flow is confined to the formations natural pores and flow channels at a bottom hole pressure less than the fracturing pressure (Figure 8). The purpose is to increase the permeability and porosity of the producing formation. This method is used primarily in sandstone formations.

During a matrix acidizing job, the contact area between the acid and the formation is very large; therefore, friction pressure increases rapidly with increased pumping rates. Due to the high friction pressures, matrix acidizing must be conducted at low injection rates, and is therefore, usually limited to removing shallow formation damage (wash jobs).

**Figure 8: Matrix Acidizing.**




(a) A matrix acidizing treatment consists of slowly injecting acid into the formation so that it penetrates into the pore spaces of the rock without fracturing the formation.




(b) Matrix acidizing is used primarily in sandstone formations to dissolve unwanted materials that have invaded the rock pores during drilling, cementing and completions operations.

After the flow channels are enlarged, the materials creating the damage can be removed from the formation with the acid as it is produced back. In treating formation damage such as mud filter cake and scale, care must be taken to treat at less than the fracture pressure of the formation to avoid fracturing past the damaged area.

For maximum penetration when matrix acidizing, the acid should have a low viscosity and low surface tension. Gelled and emulsified acids should not be used for matrix acidizing because their viscosity and interfacial tension greatly increase the injection pressures and impede the flow back of the spent acid.

In both fracture and matrix acidizing, effective stimulation depends upon the permeation of the producing formation with an extensive network of channels that will serve as a gathering system for the transport of oil and gas from the low permeability rock to the wellbore.

### 4.3.1 Matrix Acidizing Horizontal Wells.

Horizontal wells are normally targeted for thin formations with good vertical permeability and reservoirs that suffer from coning problems. Matrix stimulation of long horizontal sections have been shown to be successful compared to fracture treatments in reservoirs with relatively low permeabilities (0.5 to 1.5 md) and small vertical height (less than 50 ft). Outside of this narrow range, reservoirs where vertical wells are normally considered candidates for fracture treatments, will also require hydraulic fracturing when drilled horizontally.

When matrix acidizing horizontal wells, all aspects of job design that apply to vertical wells should be considered. Placement of fluids along the length of the horizontal section is critical to the success of any stimulation. “Bull-heading” acid into horizontal wells has generally proven to be unsuccessful. In most cases the acid has a tendency to enter the formation in a zone close to the vertical section thus, obtaining only partial stimulation.

To overcome this problem, various methods have been applied to improve the distribution of stimulation fluids along the well. These methods include chemical diverters, mechanical isolation devices, partial perforation techniques (leaving blank portions in the casing, and coiled tubing.

In general coiled tubing has proven to be the most effective method for acid washes and matrix stimulation and can be used to obtain adequate coverage. With this technique, the coiled tubing is placed at the end of the horizontal section and withdrawn towards the vertical section whilst pumping acid and diverter stages. At the same time an inert fluid is pumped down the to aid placement and reaction of the acid at the point of injection. However, the stimulation fluid is likely to follow the path of least resistance making diversion and zonal isolation essential.

This technique is better discussed in other literature (Matrix Stimulation Methods for horizontal Wells. Economedes, Naceur and Klem. JPT July 1991). However, as the section to be treated in a horizontal well can be several thousand feet long, treatment volumes will be large and particular attention should be paid to the economic aspects of such a treatment.

For example, in a vertical well a small treatment may require that 100 gallons of acid per foot of pay be pumped to remove the damage. If the zone of interest was 50 ft in length, the total volume of acid required would be 5000 gallons. If this same treatment were required for damage in a horizontal section with 1000 ft of length in pay, a "small" treatment of 100,000 gallons of acid would be required. This type of

volume and greater is commonly pumped in matrix stimulation of horizontal wells with excellent results.

Drawbacks to this method of stimulation include long acid to tubing exposure times (due to limitations on pump rate through coiled tubing), and difficulty in achieving successful diversion, particularly in limestone formations as fracturing pressures would not be exceeded.

## 5. Acidizing Damage.

Formation damage will almost always occur during an acid job, therefore, it is necessary to make certain that the stimulation benefits outweigh the negative effects of the created or existing damage, for the job to be successful. When designing an acid job, the engineer must be aware the various types of damage that can occur and take the necessary steps to prevent them. The most common types of formation damage caused during acidizing are as follows :

- Formation de-consolidation.
- Fines mobilisation.
- Reaction by-products.
- Chemical incompatibilities.
- Precipitation of iron compounds.
- Emulsions and sludges.

### 5.1 Formation De-Consolidation.

The problems and damage resulting from formation de-consolidation can be very severe. Reduced permeability due to the mobilisation of the formation material can shut off production itself. Formation sand flowing into the wellbore causes numerous problems with the production equipment that can be extremely costly.

The potential for damage due to de-consolidation depends upon the formation geomorphology, acid strength and acid volume pumped. For example, if the formation consists of 10.0 % carbonate material and this material is cementing the sand grains together, it is undesirable to dissolve all of this material with acid. Reduced HCl volumes and strengths should be used in this situation when pre-flushing ahead of mud acids.

In the case where sand grains are cemented together with clay material, reduced mud acid strengths and volumes should be considered. Full knowledge of the formation mineralogy and geomorphology is essential.

### 5.2 Fines Mobilisation.

Release and mobilisation of clay and other silicate materials can severely damage a wells productivity. Since a given volume of strong acid dissolves more formation than the same volume of weaker acid, a greater volume of insoluble fines may be released by the reaction. As the well is put back on production, the fines that have been released can migrate and bridge in the near wellbore area. Released fines can also act to stabilise emulsions. The use of non-ionic or anionic surfactants, or mutual solvents such as INFLO-40 (EGMBE) will help to water-wet these fines, thus preventing emulsion stabilisation. More importantly, if the fines become oil-wet, the ability for these fines to migrate is increased. Consideration should also be given to the use of suspending agents (MMR Acid), fines stabilising agents (FSA-1), Sandstone Acid, or in the case of fracture treatments of limestones, gelled and cross-linked acids.

## 5.3 Reaction By-Products.

When calcium sulphate in the form of anhydrite ($CaSO_4$) or gypsum ($CaSO_4.2H_2O$) is present in the formation, the problem of re-precipitation may arise. This occurs because this sulphate is less soluble in spent acid than in live acid.

Since calcium sulphate has a maximum solubility in hydrochloric acid within the range of 8.0 % to 12.0 %, its re-precipitation can be minimised by the use of high-strength treating solutions. On entering the formation, the acid solution dissolves a minimal amount of gypsum. As the acid reacts, its capacity to dissolve gypsum increases. However, the calcium chloride ($CaCl_2$) formed as a reaction by-product of acid and limestone exerts an opposite effect, resulting in an over-all stabilisation of the amount of gypsum dissolved.

In addition to decreasing the solubility of the $CaSO_4$, calcium chloride increases the viscosity of the spent acid. A 15.0 % solution of HCl, when completely reacted with limestone, becomes an 18.9% solution of $CaCl_2$. If the acid concentration had been 28.0%, the spent acid would contain 30.7% $CaCl_2$. The viscosity of the latter solution is about twice that of the first and about three times that of live 15.0% HCl. In a well with a relatively low formation pressure this increase in viscosity could reduce the rate of return flow into the wellbore, allowing insoluble material released from the formation by the treatment to settle out in the fissures and porosity of the formation, and subsequently reduce oil or gas flow.

Strong acids, when spent, will have a higher concentration of dissolved reaction by-products than a weaker acid. The solubility of other salts is usually lowered in strong spent acid. If formation water with a high sodium chloride content is encountered, precipitation of the salt may occur.

There are many reaction by-products that can form when certain minerals are dissolved by hydrofluoric acid. The amount of precipitates actually formed is highly dependent upon the bottom hole static temperature and the acid contact time in the formation.

The most well known precipitate is calcium bifluoride which is a by-product formed by the reaction of live hydrofluoric acid with calcium carbonate material found in the sandstone matrix.

$$2HF + CaCO_3 \rightarrow CaF_2 + CO_2 \uparrow + H_2O$$

Hydrofluoric acid reacting with clay materials, can form by-products such as fluosilicic acid ($H_2SiF_6$) and fluoaluminic acid ($H_3AlF_6$). These acids will react further with carbonate materials to form hydrated silica and aluminium respectively. These hydrated compounds will precipitate out of solution in volumes that are much greater than the volume of the of the original formation material dissolved, thus significantly increasing the damage potential.

$$HF + Clay \rightarrow H_2SiF_6 + H_3AlF_6$$

$$H_2SiF_2 + CaCO_3 \rightarrow \text{Hydrated Silica}$$

$$H_3AlF_6 + CaCO_3 \rightarrow \text{Hydrated Aluminium}$$

The Feldspar content of a sandstone is often overlooked. Hydrofluoric acid reacting with potassium feldspar will form a precipitating by-product of potassium hexafluosilicate. Sodium hexafluosilicate will also precipitate where a high concentration of hydrofluoric acid is reacting with sodium feldspar.

$$6HF + \text{K-Feldspar} \rightarrow K_2SiF_6$$
$$6HF + \text{Na-Feldspar} \rightarrow Na_2SiF_6$$

Amorphous hydrous silica (silicon tetrafluoride) will always be a by-product from the reaction of hydrofluoric acid with sandstone formations. This cannot be prevented, but the damage caused by it and other precipitates can be minimised with a well designed and executed acid job.

$$4HF + SiO_2 \rightarrow SiF_4 + 2H_2O$$

The following are general guidelines that can be used to minimise the damage associated with precipitates formed as reaction by-products with hydrofluoric acid :

- Use chelating and sequestering agents based on the mineralogical properties of the formation.
- Determine the hydrochloric acid (HCl) preflush and Hydrofluoric Acid (HCl:HF) volumes from formation solubility analysis, permeability and porosity.
- Overflush the acid treatment to four or five feet away from the wellbore.
- Minimise acid contact times to four hours.
- Acid strengths should be determined from the bottom hole static temperature.

## 5.4 Additive Incompatibility.

When choosing the additives to be included in an acid treatment, one must always consider the compatibility of the additives with each other and with the acid.

Solubility, dispersibility and chemical compatibility should be checked in the laboratory prior to pumping the acid system into the well.

### 5.4.1 Solubility.

Some additives are soluble in acid at low concentrations only. At high concentrations, these additives will flocculate out. If the additive is oil soluble, it will float to the top.

### 5.4.2 Dispersibility.

If an oil soluble additive is to be used, a dispersant must be added to the acid system. A good example of this is the use of xylene in acid. Without a dispersant, the xylene would simply float to the top of the acid. The dispersant must be strong enough to keep the xylene dispersed for a sufficient time for the acid to be pumped into the formation.

### 5.4.3 Chemical Compatibility.

The most common problem encountered here is the mixing of an anionic additive with a cationic additive. This can sometimes cause a precipitate to form. At times it is necessary to mix cationics with anionics, for example, retarded acids often use anionic surfactants to emulsify the acid, whilst most corrosion inhibitors are cationic. The same applies to anti-sludging agents. In these cases consideration should be given to the use of pre-flushes containing diesel or solvent to contain one of the additives.

## 5.5 Iron Compounds.

Precipitation of iron hydroxides can severely damage a well. There are two forms of iron hydroxide that need to be considered, ferrous ($Fe^{2+)}$ and ferric ($Fe^{3+}$).

Ferrous hydroxide will precipitate out at a pH of 5.0 or more, whereas ferric hydroxide will precipitate out at a pH of 2.2 or more, therefore ferric hydroxide is the main one to be concerned with. Some iron control agents are designed to reduce ferric iron ($Fe^{3+}$) to ferrous iron ($Fe^{2+}$), whilst others are designed to maintain a low pH (Acetic Acid).

The most common source of iron problems in a well are the tubulars. New tubing is covered with mill scale which is in the form of ferrous oxide (FeO) and ferric oxide ($Fe_2O_3$). Acid will dissolve and dislodge this scale from the tubing as it is pumped into the well and carry it down into the formation.

Currently used iron control agents can only effectively control up to 10,000 ppm iron. Case studies have shown that as much as 100,000 ppm of dissolved iron can be picked up by the acid in less than 9000 ft of tubing. For this reason tubing strings should always be cleaned of iron scales with a "Pickling" treatment prior to pumping acid through them and into the formation.

## 5.6 Emulsions and Sludge.

### 5.6.1 Emulsions.

Most crude oils contain natural chemicals which frequently act to stabilise emulsions formed with acid or with spent acid during a treatment. In general the tendency to form emulsions increases with the concentration of the acid. The viscosity of an emulsion, being higher than that of either its components, means that its flow from the formation into the wellbore is impeded. An added expense is the disposal of the emulsions aqueous phase once it has been produced. When designing treatments the following should be considered:

- Emulsions can be prevented if tested.
- Crude oil from offset wells can have different emulsifying tendencies.
- Over-treating with surfactants can cause an emulsion.

Production is severely hindered due to the high viscosities inherent with emulsions. Emulsions are usually very easy to prevent by selection of the correct surface acting agents and can be easily determined by simple laboratory tests. Whenever possible, emulsion tests should be carried out using crude oil samples from the well to be treated and the proposed acid treating solutions. It is often assumed that if an acid system does not form an emulsion with crude from one well in the field that it will not form one with others. Unfortunately this does not always hold true. Crude oils from offset wells can have very different emulsion forming tendencies.

### 5.6.2 Sludge.

Some crude oils react chemically with hydrochloric acid during stimulation treatments to form solid or semi-solid particles called sludge, or asphaltene sludge. This can restrict or completely plug the flow channels in the producing formation reducing the effectiveness of the acid treatment. The following can be said of acid sludges:

- Form in wells that produce asphaltic crude oils.
- Can be prevented if tested.
- Low pH destabilises the asphaltic colloidal dispersion.
- High aromatic solvents are required for removal. (Xylene or Toluene).
- Form more readily with stronger acids.

The formation of sludge when acidizing can occur in any crude oil that contains asphaltenes. In general it can be said that, if a crude oil has a tendency to sludge, it

is more likely to form with stronger acids and in greater volumes. Crude oils with this tendency can be identified by simple laboratory tests and treatments can then be designed to prevent their formation.

Sludges form when asphaltenes are precipitated out of the crude oil. Asphaltic material exists in the formation as a colloidal dispersion of minute asphaltene particles permeated by adsorbed maltenes. These maltene-asphaltene micelles are stabilised by a double electrolytic bond. The low pH environment created by acids disrupts this bond and causes destabilisation of the asphaltenes, thus allowing them to aggregate and to precipitate out from the crude oil.

Unfortunately, sludge is extremely difficult to remove because it is insoluble in most treating solutions, so most effort is directed towards prevention rather than correction. Acid concentrations as low as 1.0% have produced sludge with susceptible crudes, sludge prevention generally becomes more difficult as the concentration of the acid increases.

Sludges are very viscous and usually require the use of a high aromatic solvent (xylene or toluene) for removal. Sludge prevention procedures should be used when acidizing wells that produce asphaltenic crudes.

## 6. Introduction to Acid Treatment Design.

Wells that have skin or zonal damage are good candidates for well stimulation treatments. Major increases in productivity or injectivity can result. The well and the treatment, however, should be selected with care, and reservoir conditions should be adequate to assure economic pay-out. Misapplied stimulation treatments are costly and ineffective, often creating more problems than they solve.

Selecting the correct treatment is often not a simple matter. With an engineering approach to any well problem however, the chance of success is generally increased. The following information should be considered in the selection of a well treatment:

- Type of formation and mineral composition of the formation.
- Type and amount of damage.
- Contact time available for chemical treatment.
- Physical limitations of well equipment.
- Bottom hole pressure and temperature.
- Possible contaminants such as water, mud, cement filtrate and bacteria.
- Treating fluid compatibility with contaminants present and reservoir fluids.
- Formation properties such as acid solubility, permeability and porosity.

Various damage mechanisms and treatment design criteria are considered in the following sections.

### 6.1 Geographic Probability.

If no information other than well location and T.V.D. is available, then the only design criteria will be geographic probability. For some areas of the U.S.A. BJ-Services has developed an indexing system based on geographic probability. This system provides geological data such as clay technology and treatment response data including: PI performance, emulsion tendencies, sludging, clean-up rates, type of particles solubilised, precipitates etc.

## 6.2 Primary Considerations.

1. If formation damage does not exist, then a matrix acid treatment will probably not be economically viable.

2. The production potential must be determined. Even if damage exists, the treatment may not be economical if the production improvement potential is very small.

3. Production techniques and procedures must be evaluated to be sure that these are not hindering production. (Size of production tubing flow-lines etc.). The BJ Services “Production Optimisation Program“ (POP) can be used to help analyse for these situations.

4. Obtain information about the formation's physical characteristics and chemical properties. (Core testing and previous experience).

5. Obtain information about the properties of the formation fluids. (Water analysis and scaling tendency).

6. Determine the cause and type of formation damage.

7. Design the acid treatment to clean-up the damage and to prevent acidizing damage.

8. The treatment must be placed properly (Diversion).

## 7. Drilling, Completion and Work-over Design Considerations.

### 7.1 Drilling Considerations.

1. Was the correct type of drilling mud used.

2. What was the fluid loss of the mud whilst drilling through the zone of interest.

3. Did lost circulation occur. How many barrels of mud were lost to the formation.

4. Was lost circulation material used. If so, how much and what kind.

5. Are there extreme washouts in the production zone.

### 7.1.1 Drilling Formation Damage Mechanisms.

1. Invasion of mud particles into the formation which includes clays, barite, other weighting agents, lost circulation materials and cuttings.

2. Drilling and cement filtrate damage may result in polymer plugging, scale formation, surfactant altered wettability damage, clay swelling, clay dispersion, asphaltene deposition, and oil-mud sludging.

**Table 4: Drilling Damage Treatment Options.**

| Situation | Treatment |
|---|---|
| Mud damage, Clay swelling, Clay dispersion, Polymer Damage and Scales. | Standard HCl:HF mud acid Silt and sand suspending agents are useful. |
| Wettability damage. | Mutual Solvents and or Surfactants. |
| Sludging and Asphaltene Damage. | Paravan/Solvent Soaks. |

## 7.2 Drilling Mud Damage.

Shallow formation damage, commonly called skin damage, results when incompatible fluids and solids invade the formation. On new wells, mud solids and filtrate from the drilling fluid cause most of this contamination.

The mud filter cake deposited on the exposed formation face during drilling operations consists of solid drilling mud particles and some drill cuttings. This filter cake forms a cylindrical barrier of reduced permeability around the wellbore. Generally, the penetration into the formation of drilling solids seldom exceeds a very few inches in non vugular or unfractured formations.

### 7.2.1 Removing Drilling Mud Damage.

Laboratory tests show that acid treating solutions are most effective for removing this type of shallow formation damage. Although the acid usually dissolves only part of the mud solids, it effectively penetrates and disperses the remaining insoluble solids by reacting with the formation to which they are attached.

In removing skin damage at the wellbore, small treatment volumes at low pressures and injection rates generally are employed. Low rates allow the treating fluid to move radially and uniformly into the damaged zone for more effective clean-up.

In designing a mud removal treatment during initial well completion several factors should be considered.

- Type of mud.
- Acid Solubility of the formation.
- Type of formation.
- Length of perforated or open hole interval.

Acid solutions recommended for treating wellbore damage caused by various types of drilling muds are presented in (Table 5). Whilst this table can be used as a guide, laboratory flow tests on representative cores and fluids at corresponding temperatures should be conducted whenever possible. For example, emulsion testing will determine the correct concentration of surface acting chemicals to be used in the treating solution.

**Table 5: Recommended Treatment for Damage Removal Based on Mud Type and Formation Type.**

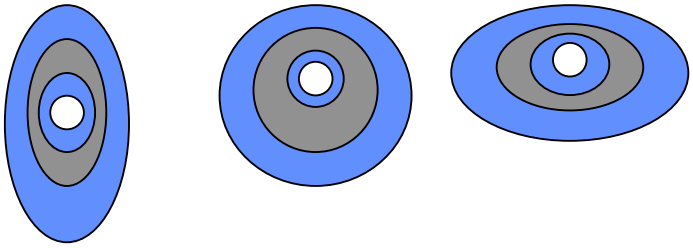
| Mud Type | Limestone - Dolomite Formations (7-1/2% - 28%)* | Sandstone Formations (5% -15%) * |
|---|---|---|
| Water Clay | Clean-up Acid<br>Regular HCl + 1.0% NE-2<br>MMR Suspending Acid<br>NE-Type Acid ** | Mud Sol; Mud Sol 15:3<br>Regular HCl + 1.0% NE-2<br>Clean-up Acid<br>HCl:HF Acid Mixes<br>Alcohol-Acid |
| Oil Emulsion | Clean-up Acid<br>Regular HCl + 1.0% NE-2<br>MMR Suspending Acid<br>NE-Type Acid **<br>One Shot Acid "Plus" (HCl) | Mud Sol; Mud Sol 15:3<br>Clean-up Acid<br>HCl:HF Acid Mixes<br>Alcohol-Acid<br>NE-Type Acid **<br>One Shot Acid "Plus" (HCl:HF) |
| Inverted Oil Emulsion | Regular HCl + 1.0% NE-2<br>NE-Type Acid **<br>One Shot Acid "Plus" (HCl) | Mud Sol<br>Regular HCl + 1.0% NE-2<br>NE-Type Acid **<br>One Shot Acid "Plus" (HCl:HF) |
| Oil Base | Kerosene, Diesel, Crude Oil Containing NE-110 and/or Acetic Acid<br>One Shot Acid "Plus" (HCl) | Kerosene, Diesel, Crude Oil Containing NE-110 and/or Acetic Acid<br>One Shot Acid "Plus" (HCl:HF) |

* Range of concentration which applies to all acid groups.
** Acid containing NE-additive, as determined by emulsion tests.

## 7.3 Drilling Fluid Damage in Horizontal Wells.

Damage around a horizontal wellbore is neither radial nor distributed evenly along its length. Variations in permeability (anisotropy), create an elliptical damage profile normal to the wellbore (Figure 9). The exposure time to fluids during drilling and completion operations will result in a truncated elliptical cone of damage along the length of the well (Figure 10), with the base of the cone nearest the vertical section of the wellbore.

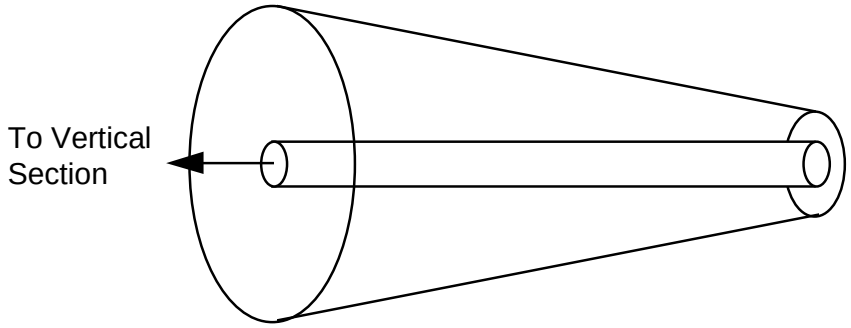
**Figure 9: Schematic of Typical Damage Profiles in Horizontal Wells.**



$I_{ani} = 0.25$ $I_{ani} = 1.0$ $I_{ani} = 3.0$

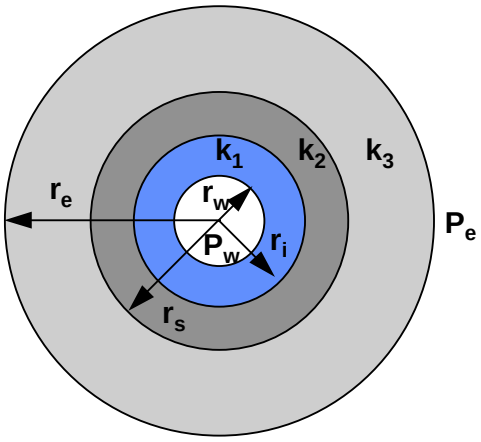
$I_{ani}$ = Permeability anisotropy variable.

**Figure 10: Schematic of Typical Horizontal Well Damage Cone.**




Diversion is often difficult to achieve in horizontal section (acid tends to take the path of least resistance), even when using mechanical diverting aids or coiled tubing. Taking the large quantities of acid required for matrix stimulation of horizontal sections into account, it is often desirable to consider only partial damage removal. This will result in the creation of a stimulated zone with improved permeability surrounded by a collar of damage (Figure 11). However, distribution of the stimulation fluid along the length of the well is still important, particularly when considering the nature of the damage distribution.

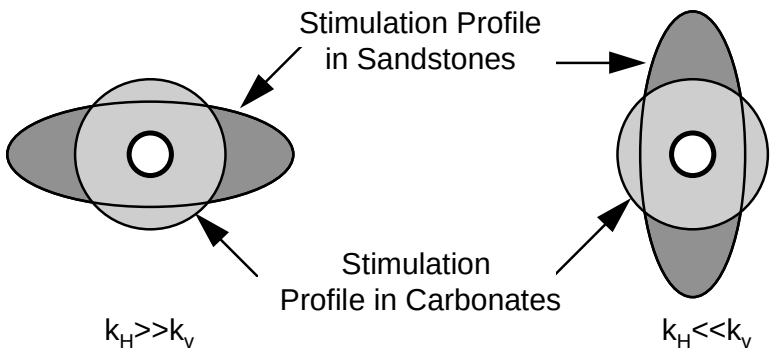
**Figure 11: Partial Stimulation With Damage Collar**.




$r_w$ Wellbore radius.
$r_i$ Radius of improved permeability (Stimulated).
$r_s$ Damage radius.
$r_e$ Drainage radius (Boundary).
$P_e$ Outer pressure boundary.
$P_w$ Wellbore Pressure.

When stimulating with coiled tubing, the rate of tubing withdrawal and the volume of fluid pumped into each section of the hole should take into account the identified shape of the damage cone present, and the type of formation to be stimulated. For sandstones, the stimulation fluid injection should mimic the shape of the damage cone, and a truncated cone of improved permeability should result with acid volumes and tubing withdrawal rates being closely related to porosity. For carbonate reservoirs, the stimulation profile under matrix conditions will be dendritic, with a wormhole network extending radially from the wellbore. The volume of acid and withdrawal rate of the coiled tubing will be related to the expected radial wormhole porosity created.

**Figure 12: Schematic of Stimulation Profiles for Sandstones and Carbonates.**




## 7.4 Cementing Considerations.

1. Did lost circulation take place during cementing. If so, how much was lost and was it lost to the production zone.

2. Was KCl or salt used in the cement slurry. (Clays, shales and formation water compatibility).

3. What was the fluid loss of the cement slurry.

4. Is there a good bond (to pipe and formation) across, above and below the productive zone (CBL).

5. Are there any channels in the cement (CBL, CET).

6. What type of cementing preflush was used.

## 7.5 Lost Circulation Materials (LCM).

1. Determine if HCl Soluble.

   - $CaCO_3$ dissolve in 15% HCl (1.84 lbs per gallon of acid)
   - $FeCO_3$ dissolve in 15% HCl (2.12 lbs per gallon of acid)

2. Determine volume of LCM pumped.

3. Calculate additional volume of HCl required to completely remove the material, this volume should be added to the required volume calculated to achieve a 2.0 ft radial penetration.

4. Acid soaks are often helpful.

5. Auxiliary nitrogen or carbon dioxide is usually required to ensure even distribution of the acid.

## 7.6 Perforating Considerations.

1. Was the casing and tubing cleaned (pickled) prior to perforating. (Mill varnish, iron oxide scale).

2. Was too much pipe dope used.

3. Was the perforating fluid filtered. If not what was the solids content.

4. Was the well perforated overbalanced. If so, with how much differential pressure.

5. Was the well perforated under-balanced. If so, with how much differential pressure.

6. What is the theoretical depth of penetration of the charge used.

7. What is the shot density. Did all the shots fire.

8. Were charge size and shot density the correct choice for the lithological characteristics.

### 7.6.1 Perforating Damage Mechanisms.

1. Perforating Overbalanced with dirty fluids.

2. Perforating Under-balanced with dirty fluids.

3. Inadequate depth of penetration, especially if penetration beyond the cement sheath is not accomplished.

4. Perforation debris, compacted or crushed zone which results in reduced permeability.

5. Diameter of perforations and the number of shots per foot. Perforation jobs should be designed to achieve as near to an open hole performance as possible (normally 12 SPF minimum). Inadequate SPF will put an undue stress on the formation matrix and cause sand production.

### 7.6.2 Perforating Treatment Options and Design Criteria.

1. Utilisation of perforation wash tool. The higher the shot density the shorter the effective wash zone must be. For example at 12 SPF wash 6.0 inches at a time.

2. Make sure that the perforating fluid was filtered, examine and retain samples if possible. If the fluids average particle size exceeds 10.0 microns, then a mud acid job is required. This is especially true prior to a Gravel Pack since this would result in "locking" the damage in place.

3. HCl acid soaks are usually ineffective at removing perforation damage unless the HCl solubility is greater than 20%.

## 7.7 New Completion Considerations.

1. Was the well killed. If so, what was the kill fluid.

2. How much volume of kill fluid was used. Was this volume completely produced back.

3. Was the kill fluid filtered. If not, what was the solids content.

4. Was the kill fluid tested for compatibility with the crude oil or with crude oil from an offset well.

5. Was the well circulated clean to Total Depth prior to being put on production.

6. Were any surfactants added to the kill fluid for surface tension reduction. Were any other chemicals used.

### 7.7.1 Completion Damage Mechanisms.

The most common cause of completion fluid damage is dirty fluids resulting from poor filtration practices and fluid incompatibility.

**Table 6: Completion Fluid Damage Treatment Options.**

| Damage Mechanism | Treatment Options |
|---|---|
| Solids invasion | HCl:Mud acid, Solids dependent |
| Clay swelling | HCl:Mud acid |
| Clay mobilization | HCl:Mud acid |
| Water block | Surface tension reduction |
| Emulsion block | Dependent on emulsion external phase. |
| Polymer Damage | EZ-Clean EnZyme Treatments |
| Wettability damage | Mutual solvents and or surfactants |
| Precipitation of solids | Solids dependent |

## 7.8 Work-over Considerations.

1. Refer to completions questions.
2. Has scale inhibitor been used. If so, is it still effective.
3. Have acid treatments been performed in the past. If so, what did they consist of and how much volume was pumped.
4. How were the previous jobs pumped.
5. Has diverting material ever been used. If so, how much and what kind.
6. Were previous treatments successful. If so, how successful in terms of production increase.
7. Have the production increases from previous acid treatments been long term.
8. Has the zone been previously fracture stimulated. If so, what volume and type of fluid were pumped .What type and volume of proppant were used. What were the treatment results.

9. What was the obtained fracture height.

10. Is the production equipment still operating properly.

### 7.9 Disposal Wells Design Considerations.

The unique aspect of disposal well treatment is that the formation damage can be isolated easily by analysing the plugging agent at surface.

**Table 7: Disposal Well Treatment Options.**

| Damage Mechanism | Analytical Procedure | Treatment Options |
|---|---|---|
| Oil and Grease Wettability Damage | Oil and grease content | Paravan<br>One Shot Acid<br>Mutual Solvents |
| Scale | Water analysis Scaling tendency | Depends on Composition |
| Iron | Iron count | HCl and Iron control |
| Bacteria | API Bottle Test<br>Biocide Screen<br>Time Kill Test | Acid, Biocide and Solvent [1] |

[1] API wettability tests should be run to verify that the biocide will not cause wettability damage.

## 8. Production Considerations.

1. Is the well's production decline curve typical for the field.
2. What is the current gas/oil ratio (GOR). Has this changed with time.
3. What is the current water/oil ratio . Has this changed with time.
4. Has the water/oil ratio changed with total produced fluid remaining the same.
5. Has the API gravity of the crude oil changed.
6. What is the current asphaltene content of the crude oil. Has this changed with time.
7. What is the current paraffin content of the crude oil. Has this changed with time.
8. Have paraffins or asphaltenes been known to accumulate at any time in the flow lines, surface equipment, production string, or perforations.
9. Have scale deposits been found. If so, where and what type.
10. Has formation sand been produced.

### 8.1 Production Curves.

As water increases:

- Formation fines plugging occurs.
- Chloride content increases, resulting in the nucleation and deposition of acid-insoluble organic deposits.
- Maltenes are stripped due to their lower melting point than that of the host asphaltene molecule, resulting in asphaltene deposition.
- Higher probability of the formation of mineral salts.

Sudden Decline:

- Mechanical Failure.
- Fines Migration

Water increases, oil decreases, but total fluids remain the same:

- Chemically altered wettability[1].
- Acid insoluble organic deposition[1].
- Depletion.

[1] This damage should be removed with low cost non-acid systems.

Increasing GOR with associated drop in API Gravity:

- Acid insoluble organic deposition.

**Table 8: Formation Damage Treatment Options for Different Drive Mechanisms.**

| Formation Damage Mechanism | Treatment |
|---|---|
| **Water Drive** | |
| Accelerated water production after acidizing. | Selective acidizing |
| Asphaltene damage | Paravan/Solvent soaks |
| Water production | Aquatrol 1,2 or 3, Direxit |
| Scale formation | Depends on composition |
| **Gas Drive** | |
| Water block | Reduce surface tension |
| Paraffin damage | Paravan/Solvent soaks |
| **Solution Drive** | |
| Water block | Reduce surface tension |
| Inadequate formation pressure | Carbon Dioxide or Nitrogen |
| Organic formation damage | Paravan/Solvent soaks |
| **Combination Drive** | All of the above |

## 8.2 Bottom Hole Temperature Design Factors.

1. Select acid strength according to Maximum Strength recommended (see Table , page 21).

2. Acid reaction rate is exponential with temperature therefore, there is a very high potential for acid attack of tubulars.

3. High temperature acidizing can result in wettability damage from corrosion inhibitors and surfactants. Use mutual solvents in the preflush. (EGMBE, INFLO-40).

4. Live acid penetration is reduced in high temperature wells due to increased acid reaction rates. This can create problems of reduced near wellbore permeability as a result of compressive strength reduction. This is caused by the total removal of the matrix binder in the formation ( for example; carbonates, silicates, clays etc.).

5. Damage from reaction precipitates is more likely in high temperature wells.

6. Chlorination of mutual solvents can occur at bottom hole temperatures above 200° F (93° C). Reduced acid strengths at these conditions will minimise this potential.

7. Corrosion inhibitor concentrations are critical at higher temperatures. Reduce the contact time and cool down the well whenever possible.

8. Acid contact times in the near wellbore area should be no more than four hours at low temperatures (less than 180° F (82° C)). At higher temperatures, contact times should be limited to the time required to prepare the well for flow back.

**Table 9: Temperature Considerations.**

| Situation | Temperatures | | | | | | |
|---|---|---|---|---|---|---|---|
| | 150°F | 165°F | 170°F | 180°F | 185°F | 200°F | 240°F |
| Emulsion Blocks | L | L | M | M | M | U | U |
| Organic Deposition | L | L | M | M | M | M | U |
| Asphaltene Coking | U | U | U | U | U | M | L[1] |
| Bacteria | L | L | M[2] | M[2] | M[2] | U | U |
| $CaCO_3$ Scale | L | L | L | L | L | L | L |
| $BaSO_4$ Scale | L | L | L | M | M | M | U |
| $CaSO_4$ Scale | L | L | L | M | M | M | U |
| Chlorination of Mutual Solvents | U | U | U | U | U | M[3] | M[3] |
| Rigid Emulsion Film | L | L | L | L | L | M | M |
| Are Retarded HF Systems Economical | L | L | M | M | M | U | U |

L = Likely M = Maybe U = Unlikely

1 API gravity must be less than 32° and asphaltene to maltene ratio should be ≥ 1:1.

2 Microbiological damage only occurs at these temperatures as a result of contaminated gel or sea water and/or surface water contact containing no biocide.

3 The lower the HCl solubility and the higher the HCl acid strength, the higher the probability of chlorination.

## 9. Formation Fluid and Rock Characteristic Considerations.

1. Are sensitive clays present. What volume and what kind of clay. What kind of clay sensitivity (Swelling, migrating, water entrapment).

2. Are iron bearing minerals present and in what volume.

3. Are feldspars present and in what volume.

4. What is the solubility in HCl Acid.

5. Is the formation consolidated or unconsolidated. What is the matrix binding or cementing material. Is the formation susceptible to sand production.

6. Is the formation geology homogeneous vertically and horizontally. What is the horizontal and vertical permeability (Anisotropy)

7. What is the porosity.

8. What is the water saturation.

9. Is there a distinct oil/water contact. Is there a distinct oil/gas contact.

10. What is the crude oil API gravity. What is the crude oil viscosity at down hole conditions.

11. What are the paraffin and asphaltene contents of the crude oil.

12. Does the crude have natural emulsifying tendencies.

13. What is the formation brine pH.

14. Does the formation water have a scaling tendency.

15. What is the bottom hole static temperature (BHST).

16. What is the reservoir pressure (BHP)

17. What is the bottom hole frac pressure (BHFP).

## 9.1 Mineralogy Design Factors.

1. If solubility in hydrochloric acid is greater than 18%, use HCl only. Do not use hydrofluoric acid (HCl:HF). (See Table 14, page 67)

2. If solubility in hydrochloric acid is greater than 10%, then the standard HCl volume of half the HCl:HF volume is usually adequate.

3. If the total clay content of the formation is less than 5.0%, then use 7.5% HCl : 1.5% HF.

4. If the total clay content of the formation is greater than 5.0%, then use 12% HCl : 3.0%. HF.

5. If iron bearing minerals are present (chomasite, siderite, haematite or pyrites), use iron control additives at volumes determined from core tests or spent acid returns. (Total iron in parts per million divided by five will give an estimate of the ferric iron content).

6. Presence of iron bearing minerals will cause asphaltene precipitation. The use of anti-sludge additives or solvent preflushes depending upon the severity of the sludging potential.

7. If chlorite clays are present, increase the iron control additive concentrations in the HCl preflush.

8. If illite clays are present and the permeability is less than 120 md, reduce the surface tension to at least 30 dynes per centimetre.

9. If the feldspar content is less than 20 %, use 12% HCl : 3% HF.

10. If the feldspar content is greater than 20 %, use 7.5 % HCl : 1.5 % HF.

11. If the formation is susceptible to de-consolidation, use low strength HCl and HCl : HF concentrations.

Clays and silts may remain to plug the permeability after sandstones and "dirty" limestones or dolomites have been acidized. Suspending Acids (e.g. MMR acid) have therefore been developed which "suspend" these undissolved particles, thereby helping to remove them from the formation. Fines stabilising agents (FSA-1) have also been developed to “lock” the fines, in particular clays, in the formation matrix.

**Table 10: Treatment Options for Formation Damage Caused by Indigenous Minerals.**

| Mineral | Potential Problems | What To Avoid | Treatment Options |
|---|---|---|---|
| Kaolinite | Mobile Fines | High Flow Rates | Rate Control.<br><5%-Acidize - Standard HCl/HCl:HF<br>>5% - Evaluate for Stress Pack |
| Illite | Mushing | Fresh Water Systems | Permeability > 120 Md Acidize - Standard HCl/HCl:HF<br>Permeability < 120 md reduce surface tension to 30 Dynes/$Cm^2$ |
| Smectite (Montmoril-lonite) | Swelling | Fresh Water Systems | Acidize - Standard HCl/HCl:HF<br>Perform Immersion Tests to see if alcohol/acid blends or other additives are necessary to prevent swelling |
| Chlorite | Iron Hydroxide Precipitate, Hydrous Silicate, Amorphous Alumino Silicate Scale | Oxygen Rich Systems: Ph>2.8 Inadequate Sequesterant. Buffered Acid Systems. | Acidize - Standard HCl/HCl:HF with properly evaluated sequestering agents, boric acid volume as required. Overflush as required |
| Mixed Layer Illite/ Smectite | Swelling | Fresh Water Systems | Acidize - Standard HCl/HCl:HF |
| Feldspars | Silica Precipitation | High % of HF Acid | > 20%- 7.5% HCl, 7.5:1.5 HCl:HF<br>< 20%- Standard HCl/HCl:HF |
| Chamosite | Iron Hydroxide Precipitate | Oxygen Rich Systems: Ph>2.8 | Acidize - Standard HCl/HCl:HF with properly evaluated sequesterants |
| Formation Fines (Feldspars, Quartz, Etc.) | Mobile Fines | High Flow Rates | Preflush - 7.5% HCl<br>Acidize - 7.5:1.5 HCl:HF + Boric Acid (Volume as required).<br>Overflush - as required. |
| Calcite, Dolomite | Calcium Fluoride Precipitation | Contact of calcium ion with HF Acid. | >18% - HCl Only.<br><18% - Standard HCl/HCl:HF |
| Siderite, Hematite | Iron Hydroxide Precipitation | Oxygen Rich Systems | Acidize - Standard HCl/HCl:HF with properly evaluated sequesterants |
| Pyrite | Iron Hydroxide Precipitate. Asphaltene Sludging | Oxygen Rich Systems | Preflush - 25 Gal/ft Xylene + 10% Acetic<br>Acidize - Standard HCl/HCl:HF with properly evaluated sequesterants |

The special suspending agents (MMR agents) can be added to many of the different acid treating systems that are designed for the removal of specific damage mechanisms for example:

- MMR Acid for fines suspension.
- Sequestering acid for iron.
- One Shot Acid for hydrocarbon deposit removal.

Both hydrochloric acid (e.g. Clean-up Acid) and hydrofluoric acid systems (e.g. Mud-Sol) have been developed for the suspension and removal of formation fines and invasion particles from mud etc.

### 9.1.1 Mineralogical Analytic Procedures.

Core Tests.

- Immersion Test : Oil/Water sensitivity.
- Clay Swelling Test.
- X-ray Diffraction : Bulk mineralogy and 2.0 micron clay analysis.
- Scanning Electron Microscope : Microtecture and mineralogy.
- Polarising Microscopy : Mineralogy of coarse-grained materials, and best method for study of grain-pore cement relationships.

## 9.2 Geological Probability.

Utilisation of 2 micron and bulk X-ray diffraction enables a catalogue to made of index rock properties. This data can be cross-matched with geographic data to formation make-up as well as treatment options.

## 9.3 Permeability Design Factors.

1. Acid Volumes see Table 12.

2. If the permeability is less than 120 md reduce surface tension of acid and flushes to 30 dynes/$cm^2$ or less to prevent water blocks.

3. If present, multiple permeabilities should be considered when designing diverter/acid stages for proper diversion and volume control.

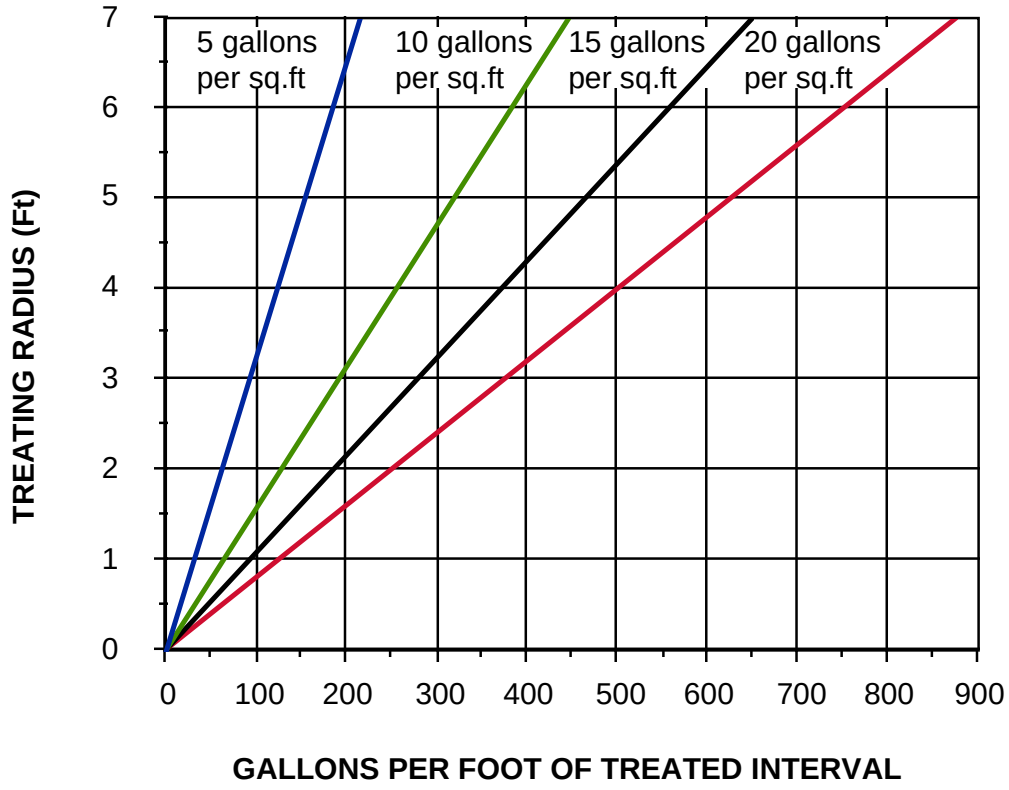
**Table 11: Acid Treating Volumes Based on Permeability.**

| Average Permeability Without Damage Ku (md). | Normal HCl Range Gal/ft (L/M) | Normal HCl:HF Range Gal/ft (L/M) | Comment |
|---|---|---|---|
| **< 0.1 md** | 15-25 (185-310) | Not Recommended | 1,3,4 |
| **0.1 - 1.0 md** | 25-50 (310-620) | 35-50 (430-620) | 1,3,4 |
| **1.0 - 10 md** | 35-75 (430-930) | 75-100 (930-1240) | 3 |
| **10- 50 md** | 50-100 (620-1240) | 100-150 (1240-1865) | 3 |
| **> 50 md** | 50-100 (620-1240)<br><br>Formic Acid 100 (1240) | 100-200 (1240-2480) | 2 |

1) Volumes should be selected based on core tests.
2) Volumes can exceed 100 gallons per foot if necessary without releasing excessive fines.
3) Volumes can be modified if indicated by field test results
4) Use acid for perforation cleaning only.

Laboratory and pilot test data are converted for field use by expressing the recommended treating volume as gallons per square foot (see Figure 6, page 23). In the laboratory a known volume of treating fluid is flowed across a given cross-sectional area of a core sample. The are to be treated in field applications is determined by the radial area of the edge of the treating radius. Once the radial area is determined, it is multiplied by the recommended treating volume (in gallons per square foot) and by the height of pay zone interval to be treated. In order to simplify these area calculations Figure 13 can be used.

**Figure 13: Recommended Treating Volume of HCl:HF in Gallons Per Square Foot of Pay.**




Example :

| | | | |
|---|---|---|---|
| Treating Radius | = | 5.0 | feet |
| Recommended Treating Volume | = | 20 | gallons per sq.ft. |
| Treated interval | = | 10 | feet |
| From Figure 13 Gallons per foot of treated interval | = | 630 | gallons |
| Volume of HCl:HF required = (630 x 10) | = | 6300 | gallons |

In estimating the damage radius of a well in the absence of well test data the following can be used as a guide to estimate treating volumes and pump rates:

- Permeability is 5.0 md or less - assume damage zone thickness to be 3.0 inches. (Refer to Table 12).
- Permeability is greater than 5.0 md - assume damage zone thickness to be 6.0 inches. (Refer to Table 13).

**Table 12: Volume of 12:3 HCl:HF Required to Treat a 3.0 Inch Damage Radius - Gallons Per Foot of Pay.**

| Pump Rate BPM/ft | Temperature | | | |
|---|---|---|---|---|
| | 100° F | 150° F | 200° F | 250° F |
| | Gal/ft | Gal/ft | Gal/ft | Gal/ft |
| 0.001 | 70 | 80 | 100 | 120 |
| 0.005 | 50 | 65 | 75 | 80 |
| 0.010 | 50 | 55 | 65 | 75 |
| 0.025 | 50 | 50 | 55 | 65 |
| 0.050 | 50 | 50 | 50 | 50 |
| 0.100 | 50 | 50 | 50 | 50 |
| 0.200 | 50 | 50 | 50 | 50 |

**Table 13: Volume of 12:3 HCl:HF Required to Treat a 6.0 Inch Damage Radius - Gallons Per Foot of Pay.**

| Pump Rate BPM/ft | Temperature | | | |
|---|---|---|---|---|
| | 100° F | 150° F | 200° F | 250° F |
| | Gal/ft | Gal/ft | Gal/ft | Gal/ft |
| 0.005 | 350 | 350 | 350 | 350 |
| 0.010 | 275 | 350 | 350 | 350 |
| 0.025 | 225 | 300 | 350 | 350 |
| 0.050 | 175 | 250 | 325 | 350 |
| 0.100 | 140 | 200 | 260 | 320 |
| 0.200 | 130 | 160 | 210 | 260 |

## 9.4 Porosity Design Factors.

In sandstone matrix acidizing, the formation porosity is used for volume calculations only:

1. The post-flush or overflush volume should be calculated for 4.0 to 5.0 feet of radial penetration based on porosity.

2. Porosity can be used to determine penetration of the live HCl if the solubility in HCl is known. If HCl solubility is greater than or equal to 10.0% then the standard HCl volume of half the HCl:HF volume is usually inadequate to prevent precipitation of reaction by-products.

3. HCl volume is based on HCl solubility. The HCl preflush volume should be sufficient to remove all HCl soluble material in a two foot radius from the wellbore.

4. HCl:HF volume requirements should be calculated based on a four hour contact time. Any longer contact time in the near wellbore area will result in damaging precipitates.

Where the formation damage is suspected to be shallow (0 to 2.0 feet) an estimate of the treating volume of acid required can be obtained from Figure 14 based on treating radius and formation porosity.

Where it is suspected that damage is deep (greater than 2.0 feet) the following equation can be used to estimate the volume of acid required:

$$\text{Pore Volume} = 3.142 \times R^2 \times H\,(P) \times 7.4806$$

Where:

R = Treating Radius in Feet.
H = Formation Height in Feet
P = Porosity Expressed as a Decimal.

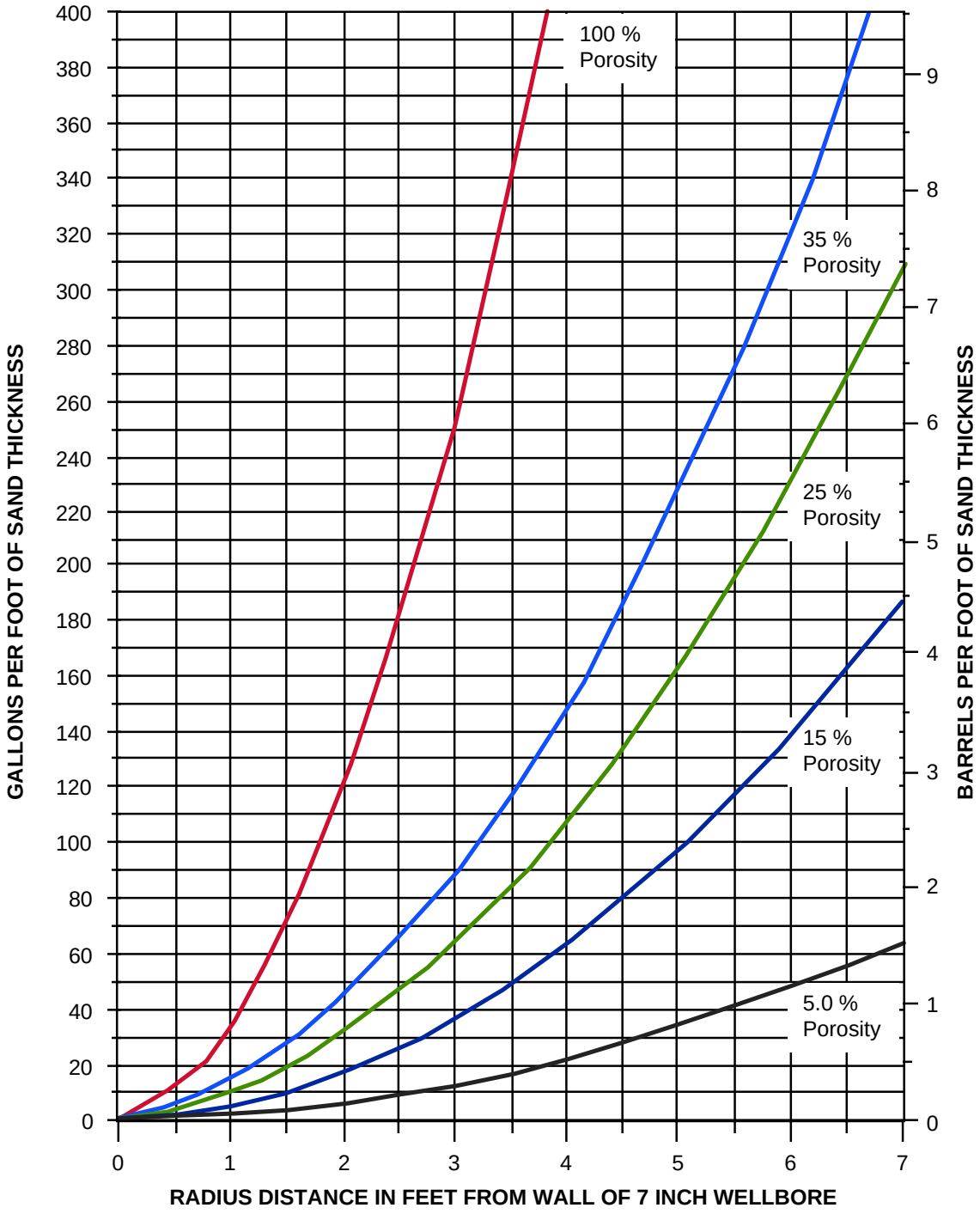
Example: 20 vertical feet of 15% porosity formation, with a required treating radius of 7.0 radial feet.

$$\text{Pore Volume} = 3.142 \times (7)^2 \times 20 \times 0.15 \times 7.4806$$

$$= 3455 \text{ gallons}$$

$$= (173 \text{ gallons per foot of pay})$$

**Figure 14: Gallons Per Foot of Treating Fluid for Differing Porosities.**



## 9.5 Reservoir Solubility.

As a general rule, formations of less than 10.0 per cent solubility are not usually stimulated with hydrochloric acid. However, hydrochloric acid may be applied to any type of formation to remove "skin damage". Nevertheless, there are exceptions to this rule. For example, if the soluble section of the formation is a sand consolidating material, acidizing results may be less effective than when limestone or dolomite "stringers" are present. This is true even where the limestone or dolomite is of low solubility.

Limestone and dolomite formations react at high rates with hydrochloric acid and at moderate rates with formic and acetic acids. The reaction of sandstone formations with these acids, however, is limited to the amount of calcareous material present in the formation. Hydrofluoric acid on the other hand, reacts with sandstone, silt, clay and most drilling muds, and has been found to be effective in stimulating sandstone reservoirs.

Note, that all acid stimulations using hydrofluoric acid should be preceded with a preflush and followed with a post-flush to prevent precipitation of reaction by-products. Formulations for the acid treatment of sandstone reservoirs based on carbonate content are given in Table 14.

Factors to be considered when choosing the appropriate acid strength are:

- Reaction time of active acid within the formation.
- Corrosion of tubular goods.
- Formation Solubility.
- Reaction product effects.
- Sludging and emulsion forming properties.
- Etch pattern on the formation
- Compatibility of demulsifier with formation and other products in the treating solution.

To benefit from an acidizing treatment, all or part of the formation being treated must be acid soluble. Solubility is a measure of that fraction of the formation that will react with an acid treating solution expressed as a percentage. Although no theoretical basis has been developed for the figures given in Table 16, there is general agreement that low formation solubilities call for low acid strengths and high formation solubilities call for high acid strengths. The figures in Table 16 summarise current field practice.

**Table 14: Acid Selection Based on Formation Carbonate Content and Temperature.**

| Percentage of Carbonate in the Formation | | | | | |
|---|---|---|---|---|---|
| **Temp °F (°C)** | **< 5.0%** | **5.0 to 15%** | **Temp °F (°C)** | **10 to 15%** | **> 15%** |
| | **Treatment** | **Treatment** | | **Treatment** | **Treatment** |
| < 200 (93) | 50 gal/ft (620 L/M) 15% HCl followed by HCl: HF | 75 gal/ft (930 L/M) 15% HCl followed by HCl: HF | < 250 (121) | 75 gal/ft (930 L/M) 15% HCl then wash perforations with HCl: HF | 100 gal/ft (1240 L/M) 15% HCl |
| 200-250 (93-121) | 35 gal/ft (430 L/M) 7.5% HCl followed by HCl: HF | 50 gal/ft (620 L/M) 7.5% HCl followed by HCl: HF | | | |
| 250-350 (121-177) | 35 gal/ft (430 L/M) 10% Formic Formic:HCl or Formic:HF | 35 gal/ft (430 L/M) 7.5% HCl + 10% Formic followed by Formic:HF | 250-350 (121-177) | 50 gal/ft (620 L/M) 7.5% HCl + 10% Formic | 50 gal/ft (620 L/M) 7.5% HCl + 10% Formic |
| >350 (177) | 35 gal/ft (430 L/M) 10% Formic or Formic:HF | 35 gal/ft (430 L/M) 10% Formic followed by Formic:HF | >350 (177) | 35 gal/ft (430 L/M) 10% Formic | 35 gal/ft (430 L/M) 10% Formic |

**Table 16: Acid Strength Based on Formation Solubility in HCl.**

| Formation Solubility % (Percentage) | Acid Strength % Percentage) |
|---|---|
| 0 -10 | 3 - 5 |
| 10 - 20 | 5 - 7.5 |
| 20 - 40 | 7.5 - 10 |
| Greater than 40 | 10 - 28 |

### 9.6 Acid Insoluble Organic Deposits.

Acid insoluble organic damage can occur in all phases of the life cycle of a well, which include:

- Drilling and Cementing.
- Completion and Work-over.
- Production.

### 9.6.1 Drilling and Cementing.

Organic deposits can form where:

1. Thermodynamic cool-down occurs, and the formation fluids reach their cloud point with insufficient BHT for thermal recovery.

2. Utilisation of aliphatic oil-based muds can result in asphaltene precipitation.

3. High pH filtrate upsets the double-bonded electrolyte which stabilises the asphaltene/maltene aggregate.

### 9.6.2 Completion and Work-over.

Organic deposits can form due to:

1. Thermodynamic effects, as with Drilling and Cementing.

2. The use of high chloride brines, which can result in the creation of nucleation sites for the branching of paraffins and asphaltenes.

3. The use of incompatible solvents (such as diesel), which can cause the instantaneous precipitation of asphaltenes.

### 9.6.3 Production.

When a virgin reservoir is initially completed, the formation fluids are in complete physical and chemical equilibrium. However, as production begins, the “light ends” (solvent) are preferentially produced, leaving the heavier molecular weight components (solute) behind. Therefore the longer a well is produced, the higher will be the probability of acid insoluble organic deposition.

### 9.6.4 Organic Deposit Damage Mechanisms.

1. As water production increases, chloride nucleation and maltene stripping result in paraffin and asphaltene deposition.

2. The longer the well is produced, the higher the thermal sensitivity becomes.

3. Deposition naturally occurs in the production phase, in-situ, as a result of Brownian Motion and shear diffusion.

4. Asphaltene coking can occur at elevated temperatures.

### 9.6.5 Organic Deposits Treatment Options.

1. Pump 25 to 50 gallons per foot of xylene and/or toluene combined with appropriate commercial solvents, dispersants or inhibitors, (Paravan Treatments) as indicated by solvent solubility tests. Soak times of four hours or more are often required.

2. If diversion is needed and/or Auxiliary acid treatments are to be pumped, then water dispersible paraffin and asphaltene solvents should be included.

### 9.6.6 Organic Deposit Analytical Procedures.

1. Thermodynamic modelling, using gas/liquid chromatography, can aid in determination of cloud point (damage potential) and melting point (thermal recovery). Solvent extraction is also an accepted method.

2. Solvent solubility tests utilising samples of sludge or synthesised sludge can be carried out. The sludge can be packed onto pre-weighed stainless steel screens or melted onto the sides of pre-weighed jars. The sludge is then soaked in various solvent-chemical

systems for 4 hours. The solvent is then removed, the sludge dried and weighed. The optimum system can be determined by this method.

3. Water dispersibility tests. The acid system is treated with water-dispersible solvents. Sludge samples are then added to the sample jar and heated to melting point. The samples are then placed in a shaker and dispersibility and sludge prevention are monitored.

## 10. Fluid Design Considerations.

### 10.1 Pipe Pickling Treatment Design Factors.

1. If there are no guidelines being followed for pipe dope application, use 50 gallons of xylene per 1000 feet of tubing.

2. Use 100 gallons of 15% HCl per 1000 ft of tubing if the tubing is new or has been used for water injection.

3. Circulate the xylene ahead of the acid down the tubing and out of the annulus.

4. If the reservoir pressure is too low for circulation, foam the acid and displacement fluid.

5. A pickling treatment would not be necessary if a concentric treating string is used, or if a replacement treating string is used.

6. Repeating pickling treatments on production strings is unnecessary. It may be necessary on injection wells.

7. If a pickling treatment cannot be done, highly sequester the HCl preflush or use a highly sequestered acid ahead of the preflush.

8. Alternatively, if a pickling treatment cannot be done, a spearhead of xylene dispersed in highly sequestered HCl will address any pipe dope accumulations.

### 10.2 Preflushes.

Preflushes are often used ahead of an acid treating solution, to prepare or condition the formation, so that it will accept the acid in the most favourable sections and without creating damage.

Several acid systems have been developed where preflushes are required. The Spearhead Acid Control (SAC) technique employs an aqueous spearhead to create fractures and place a temporary protective film on the face of the fractures. This film restricts leak-off and aids in the deep penetration of live acid.

Selective acidizing formulations (SAF) employ a specially treated kerosene or diesel oil preflush. The preflush allows the formation to react with acid in the oil producing interval whilst restricting the invasion of acid into the water producing strata.

In stimulating sandstone formations, it is generally recommended that the hydrochloric and hydrofluoric acid mixtures be preceded by a preflush of

hydrochloric acid commonly at a concentration of 15% HCl (See Figure 15). This preflush serves two purposes:

- It dissolves carbonates in the formation so that the following hydrofluoric acid will remain active to dissolve the clays and silicates.
- It removes calcium compounds, minimising the formation of insoluble precipitates.

(Refer to Tables Table 14 and

Table, page 67 for other requirements).

Figure 15 can be used to calculate the required volume of 15% HCl Preflush required for a sandstone stimulation based on formation solubility and treating radius.

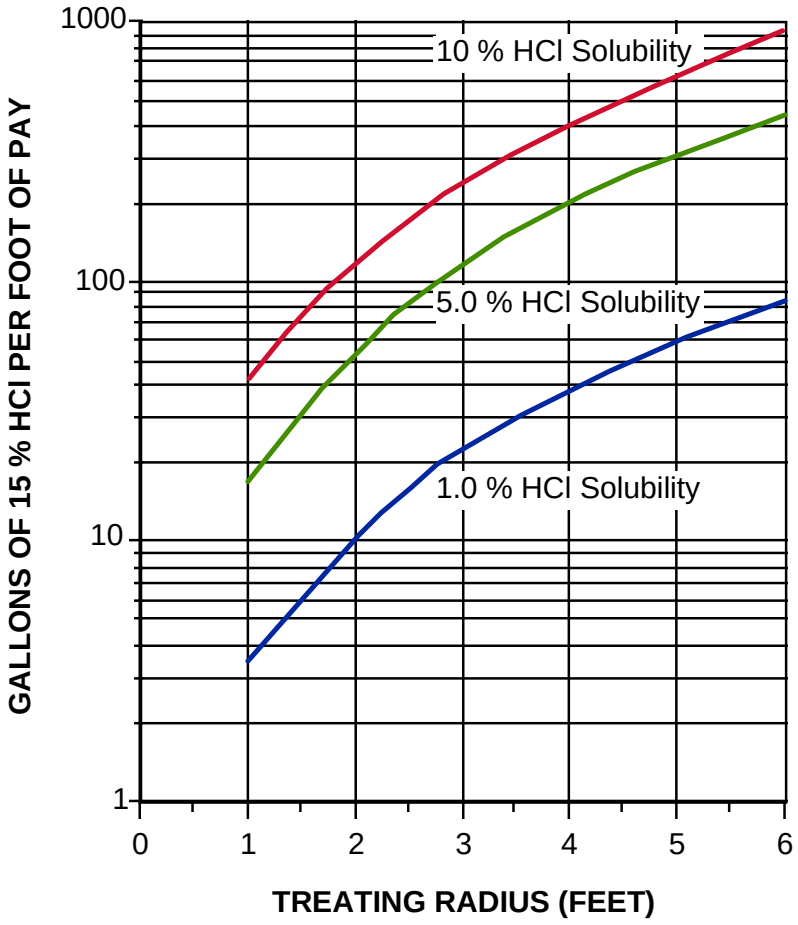
Example :

10 feet of pay zone with a solubility in HCl of 5.0%.
Required treating radius is 5 feet.

From Figure 15:

| | | |
|---|---|---|
| Gallons of 15% HCl required per foot of pay | = | 310 gallons |
| For 10 feet of pay | = | 310 x 10 |
| Volume of preflush required | = | 3100 gallons of 15% HCl |

**Figure 15: Recommended Preflush Volume in Gallons of 15% HCl Per Foot of Pay for Various Radii.**




Other preflushes include:

- Aromatic solvents and diesel for removal of hydrocarbon deposits or as carrier fluids for acid retarders and anti-sludging agents.
- Mutual solvents and alcohols, for the prevention and removal of water blocks, improved clean-up and water-wetting, and where clay minerals are present.
- Hydrochloric acid for the prevention of precipitation of acidizing by-products with hydrofluoric acid (see section 3.2.2., page 24).

### 10.2.1 Preflush Design Considerations.

1. When acidizing sandstones, iron control additives are most critical here because iron bearing minerals are highly soluble in HCl. The ensuing mud acid treatment will come into contact with less iron because these minerals will have been removed (Ferrotrol Agents).

2. Iron control additives are also important because the preflush will remove any iron scales from the tubulars and carry the into the formation.

3. If asphaltenes are present, it is important to use Anti-sludging additives in the preflush (NE-32, ASA-251, MSS-100). This is the fluid that will come into contact and mix with the crude oil in the greatest volumes. It is therefore more likely to cause a problem with asphaltenes.

4. A solvent wash ahead of the HCl preflush may be necessary to control sludging. (Xylene, Toluene, Diesel).

5. If carbonate scales have been deposited in the matrix, the preflush should be a solvent/acid dispersion (One Shot Acid). If the scale is the only damage mechanism involved, mud acid should not be used.

6. Use a preflush of hydrochloric acid when treating sandstones with mud acid (hydrofluoric acid). The preflush prevents brine contact with the mud acid and potential precipitation of by-products.

7. As a general rule of thumb, the HCl preflush volume should be half the volume of the mud acid treatment, if the HCl solubility is less than 10.0%. If the HCl Solubility is from 10.0% to 18.0%, the volume should be calculated for removal of all HCl soluble material within a two foot radius of the wellbore. (Refer to Table 14 page 67).

## 10.3 Diverting Treatment Options and Design Criteria.

To obtain the best results from most acid stimulation jobs it is important that the acid be distributed over the entire production or injection interval. Without some method of diverting an acid treating solution, most of the acid will enter the most permeable, and often least productive sections of the formation, leaving parts of the producing zone un-stimulated. The following are guidelines for diverting:

1. Use mechanical diverting whenever possible.

2. Diverting before a gravel pack should utilise sand and HEC polymer only.

   - Divide the zone into treatment stages.

If the zone is less than 80 feet, base the treatment on 20 ft stages.

If the zone is greater than 80 feet, base the treatment on 30 ft stages.

- Sand concentration should be 1.0 to 2.0 pounds per gallon.

  New completions will require 12.5 pounds of sand per foot of perforations. Re-completions will require 25 pounds of sand per foot of perforations.

- When the diverter stage reaches the cross-over tool, rate should be increased to 8.33 ft/second.

Example : 60 ft Zone New Completion.

| | | |
|---|---|---|
| Step 1 | : | 1000 gallons HCl |
| Step 2 | : | 2000 gallons HCl:HF |
| Step 3 | : | 3000 gallons 3% Ammonium Chloride |
| Step 4 | : | 6 barrels HEC containing 250 lbs 40-60 sand |
| Step 5 | : | Repeat 1, 2, 3, 4 |
| Step 6 | : | Repeat 1, 2, 3 |
| Step 7 | : | Pump Gravel Pack System. |

**Diverting all other conditions.**

General Best Results:

| | | |
|---|---|---|
| Oil wells | : | Oil soluble Resin. |
| Gas wells | : | 65 Quality Foam. |

### 10.3.1 Foam Diverting Techniques.

When using foam diverting techniques, the first stage of the acid solution is injected into the formation as in a conventional acidizing job. This is followed by an aqueous solution of a foam producing surfactant which is displaced into the formation with a compressed gas such as carbon dioxide or nitrogen. Parts of this surfactant adheres to the rock, both in fractures and within the matrix. When this retained solution mingles with and is agitated by the following stream of nitrogen, foam is formed.

As the procedure continues and additional foam is generated, its resistance to continued movement through fractures and rock matrix increases until the pressure required to sustain additional flow is greater than the pressure required to break down another section of the interval. At this point the rate of injection into the original section is reduced, and the newly opened section accepts the next portion of acid.

This procedure is repeated as many times as necessary to stimulate the entire producing zone.

Alternatively, compressed gas is injected into the aqueous fluid stream containing the foaming surfactant at surface and foam is created. As the foam follows the acid pad into the formation the effects of multiple phase flow (liquid and gas) creates resistance to flow and results higher pressures. The higher pressure breaks down further sections of formation and the newly opened section accepts the next portion of acid.

The advantages of foam diverting techniques over conventional diverting methods using solid blocking materials are as follows:

- Foam produces a block within the formation rather than a solid block at the well bore. It contains no solid particles thus reducing potential for damage to permeability.
- The compressed gas aids in cleaning silt and undissolved particles from the formation and in the clean-up of fluids.
- Adaptability to a wide range of temperatures 70 °F to 350 °F.

### 10.4 Selective Acidizing (Water Stimulation Prevention).

Since acidizing solutions preferentially enter water bearing formations, increased production of water is an unwelcome by-product of many stimulation jobs. When the water contact is in the perforated interval, then selective acidizing should be employed to prevent accelerated water production after treatment. When applying the selective acidizing technique, the acid is diverted into the oil bearing zone, resulting in increased oil production, whilst water production remains the same.

**Table 17: Selective Acidizing Treatment Options.**

| Situation | Treatment |
|---|---|
| Oil Well - Non Gravel Packed | SAF Mark II |
| Oil Well - Gravel Packed | SAF |
| Gas Well | 65 Quality Foam Preflush |

The principal component of the SAF (Selective Acidizing Formulation) system is a specially treated kerosene or diesel oil (not crude oil) preflush, usually a minimum of 500 gallons in volume. This preflush is injected ahead of a conventional acid stimulation treatment. Preceding the preflush is a spearhead volume of 5.0 barrels of clean, water free crude oil, kerosene, or diesel oil. Between the preflush and the

conventional acid is a pad volume of 2.0 to 5.0 barrels of clean water free crude oil, kerosene or diesel oil. The spearhead and the pad prevent the preflush from contacting any water based fluids and precipitating prematurely, prior to entering the water bearing zone.

With the pay zone isolated by packers or bridge plugs, the SAF preflush enters the formation as a low viscosity fluid. Upon contact with any water in the formation, the preflush immediately forms an oil soluble precipitate at the water-SAF interface. This oil soluble precipitate will partially penetrate and effectively plug the permeability of the water producing strata. With this strata effectively plugged, the acid treatment is diverted into the oil producing strata. When the treatment is complete, the well is shut in and produced in the conventional manner. SAF systems can be used with any type of acid, with any formation and in all wells except dry gas wells.

## 10.5 Post-Flush Design Considerations.

1. Use Ammonium Chloride at a concentration that is compatible with the formation (2.0 to 4.0%).

2. If damage from precipitation of reaction by-products is suspected, consider using 3.0% HCl as the post-flush for greater pH control.

3. Use 5.0% to 10% mutual solvent for wettability (INFLO-40). This is most important when high concentrations of corrosion inhibitor have been used.

4. The post-flush prevents the mixing of the displacement fluid (brine) with the spent HCl : HF acid.

5. Use sufficient volume to over-displace the acid treatment to between 4.0 and 5.0 feet radially.

## 10.6 Over-flushing.

Over-flushing is the displacement of the acid treating solution with more than the volume of fluid required to clear the tubing and casing. This procedure is sometimes desirable and often necessary.

For example, when using retarded acid systems, the reaction time can be longer than the injection time. Greater penetration may then be obtained by over displacing the acid. The exact amount of over-flush used is related to the reaction time of the acid, therefore, for maximum penetration, just enough overflush should be used to keep the acid moving within the formation until it spends.

Occasionally it is not convenient to flow back the well immediately after acidizing. In such cases, the treating fluid should be over-flushed with water or brine to reduce the contact time of live acid on the tubing and casing.

An over-flush with hydrochloric acid is recommended in injection wells that are stimulated with mixtures of hydrochloric and hydrofluoric acids. The over-flush helps prevent plugging precipitates from forming until the acid treatment has been displaced away from the critical region of the near well-bore (4.0 to 5.0 feet), thus reducing the effects of this damage.

### 10.7 Retarded Acid Systems.

Retarder techniques are used to improve the effectiveness of acidizing treatments by slowing the rate of reaction with the formation to achieve placement of live acid deep into the formation. These treatments are normally considered in fracture acidizing of limestone or dolomite formations. Six types of retarded acid systems are available :

- Emulsified acid.
- Chemically retarded acid.
- Organic acids.
- Mixtures of organic acid and hydrochloric acid.
- Gelled Acid.
- Cross-linked Acid.

In order to effectively retard an acid system, an understanding of the factors effecting the rate of reaction of an acid must be considered.

#### 10.7.1 Reaction Rate Considerations.

The rate of reaction between an acid and a soluble formation depends primarily upon the following factors:

- Temperature of the formation during treatment.
- Pressure within formation during treatment.
- Type and concentration of the acid used.
- The kind of formation with which the acid reacts and the purity of the formation.

Two other related factors are the volume of acid available per unit of soluble formation surface area and the rate of shear (agitation) within the acid. The rate of shear through a fracture depends on the velocity of the acid and the width of the fracture.

Higher reaction rates may be employed to remove local well-bore damage, but a slower reaction is preferred for fracture acidizing. The intrinsic reaction rate of an

acid cannot be changed, but it can be effectively controlled by emulsifying the acid in oil or by interposing a film of oil between the acid and the formation such as in Super retarded acid (SRA) systems.

The effectiveness of an acidizing treatment, to improve the production from any well, depends essentially on the ability of the acid to reduce resistance to flow of the oil or gas from the formation to the well-bore.

Acid treatments may over come or reduce many kinds of flow resistance found in production or injection wells such as:

- Naturally low permeability of the formation.
- Limited conductivity of natural and induced fractures.
- Formation damage caused by drilling mud or clay swelling. Reduced permeability in the vicinity of the well bore due to formation of scale deposits.
- Reduction of effective tubing diameter resulting from the accumulation of scales.

The rate at which acid reacts with the impeding material becomes more important as the acid's distance from the wellbore increases. A high reaction rate is desirable for removing scale, which is usually formed at or near the wellbore. However, when using fracturing pressures to treat a formation, a slower reaction rate is preferred in order to enable deep penetration of the live acid. The increase in production from induced fractures or the etching of natural fractures by acid depends upon three factors :

- Increased permeability.
- Length of zone of increased permeability from the wellbore.
- Width of resulting fractures.

If the conductivity is not increased appreciably after treatment, deeper penetration of live acid accomplishes little. If the fracture faces are etched effectively, and the zone adjacent to the fractures has increased permeability, deeper penetration into the available drainage area can raise the “production increase ratio” significantly. However, it should be noted that the "rate" of improvement decreases with depth of penetration.

### 10.7.2 Measuring Reaction.

Generally the rate of reaction between limestone and acid is measured by the rate of change in the amount of available acid. In conducting a laboratory test, small samples of acid are drawn from the reaction vessel and titrated. The fraction of available acid consumed in the reaction is then plotted against elapsed reaction time. Since the basic rate of reaction on a given formation at a particular temperature and pressure depends upon the acid concentration, the last part of the reaction can be much slower than the first part. For practical reasons, the end of

reaction is taken as the time at which 90% of the acid has reacted rather than 100%. (See Figure 2 to Figure 5 on pages 16 through 19).

### 10.7.3 Controlling Reaction Time.

The reaction rate of the acid on the formation can be retarded by changing the properties of the acid treatment. Acid systems can be retarded by chemical and physical means or by mixing HCl with organic acid.

Some acids, particularly the organic acids, react more slowly than hydrochloric acid. As there is no known way to change the intrinsic rate of reaction between a particular acid and a soluble rock, it is necessary to introduce "interfering" agents to reduce the rate. This is accomplished by reducing the effective area of contact between the acid and the soluble formation by:

- Emulsifying the acid in oil
- Interposing an oil film between the acid and the formation.(Chemically Retarded Acids)
- Gelling or Cross-linking the acid.

The effective reaction rate of some acids may be reduced by dissolving them in non-polar solvents (such as the lower alcohols) or in mixtures of this type of solvent and water. This method is not in general use because of the cost of non polar solvents.

Rate of reaction is related to the rate of diffusion of hydrogen ions and reaction products through the solvent containing them, therefore, increasing the viscosity of the solvent decreases the reaction rate (Gelled and Cross-linked Acids). This may be accomplished by means of certain organic gelling agents or by the use of inorganic salts. Some surfactants also act to retard the effective reaction rate.

## 10.8 Emulsified Acid.

Physically retarding HCl acid by emulsifying the acid with kerosene or diesel. This method accomplishes retardation by placing an external phase of hydrocarbon around droplets of the acid thus reducing the effective contact area with the formation. This method is by far the best means of retardation.

Emulsified Acid of acid reacts slowly with the formation, permitting deep penetration. It is generally used at fracturing pressures, where, it cleans out and enlarges existing fissures and also creates new ones. Because of its viscosity, emulsified acid carries sand effectively and can also be used as a fracturing fluid.

In an emulsion of acid and kerosene or diesel oil, the droplets of acid are surrounded by a continuous body of hydrocarbon. This decreases the effective area of contact so that less acid is reacting upon the formation at any moment in time. When the acid at the surface of the formation has reacted, it must be replaced by

live acid brought there by diffusion and convection. These processes take place more slowly through hydrocarbon than they would through a "more fluid" medium, thus reducing the reaction rate of the acid.

An emulsion of one liquid in another is created by bringing the two liquids together and physically breaking up the one to be dispersed by mechanical agitation. In well stimulation, stable emulsions are relatively simple to produce. The continuous phase (usually kerosene or diesel fuel) is placed in a tank with a stabilising surfactant that may also serve to partly control the extent of retardation.

The acid is then jetted into the tank through a hose, producing an initial emulsion that is relatively fluid. Further dispersion of the acid is accomplished by circulating the emulsion through a pump and back to the tank. The final product has the appearance of a rather thin mayonnaise. The viscosity of the emulsion increases as the acid droplets are made smaller by agitation and as the proportion of acid is increased.

BJ Services Emulsified Acid System and SRA-3 are emulsified acids used for fracture stimulation of carbonate formations. Both have a very slow reaction rate with medium to high viscosity for leak-off control.

### 10.9 Chemically Retarded Acid.

Chemically retarding Hydrochloric acid is accomplished by the addition of special surfactants designed to give a retarded reaction rate on low or high temperature carbonates.

Sta-Live acids are chemically retarded acids which have low viscosity (about the same as that for regular hydrochloric acid). This type of system is recommended for treatments where the following apply:

- Highly soluble formations.
- Wells with high bottom hole temperatures.
- Where large treatment volumes are required.
- Where low injection rates are indicated (matrix acidizing).

Super retarded acid systems are a mixture of hydrocarbon oil (kerosene or diesel), 15% hydrochloric acid, surfactant and corrosion inhibitor. The primary function of the surfactant is to stabilise a film of oil at the interface between the acid and formation. This film acts as a two way barrier through which the acid molecules migrate to the formation and through which the molecules of the acid reaction products in turn pass back to the body of the acid.

Sta-Live acid systems are chemically retarded systems designed for use with carbonate formations. These systems retard acid reaction by the chemical adsorption of a surfactant (SLA-48) on the formation face which delays the contact with the acid. These acids have low surface tension and viscosity and are generally

used to treat dry gas wells where the use of hydrocarbon preflushes or acid mixtures have proven detrimental to production.

### 10.10 Organic Retarded Acids.

Only two organic acids, acetic and formic, have been used to any extent in well stimulation. Both these acids have the characteristic of relatively low reaction rates without the addition of additives. However, due to the additional cost neither has been widely used as a replacement for hydrochloric acid systems.

Acetic Acid.

Acetic acid is usually used in the range of 5.0% to 20% concentration . In this range 1.7 gallons of acetic acid will dissolve the equivalent of 1.0 gallon of hydrochloric acid. Acetic acid has the advantage of low corrosion rates with steel, and at temperatures below 200 °F (93 °C), no inhibitor is required where contact with the pipe is less than three hours. With inhibitors, acetic acid is used as a breakdown fluid and can be placed in the well prior to perforating. The low corrosion rate without the need for inhibitors allows the use of this acid for stimulating water wells for domestic consumption.

Formic Acid.

The properties of formic acid are generally between those of acetic and hydrochloric acids of the same strength. Normally, formic acid is used in concentrations of 10% or less due to the low solubility of reaction products formed. At a 10% concentration, 1.3 gallons of formic acid are required to dissolve the same quantity of carbonate as 1.0 gallon of 10% hydrochloric acid.

#### 10.10.1 Mixtures of Organic acid and Hydrochloric acid.

Mixtures of acetic and hydrochloric acid (Super Sol, EQH acids) are used as a compromise between the greater dissolving capacity of HCl and the slow reaction of acetic acid. These delayed reaction acids are normally used in fixed ratios of Hydrochloric to acetic acid (9:1, 8:2, 7:3, and 5:5). A ratio of 9:1 hydrochloric:acetic acid is the fastest reacting of these mixtures. The dissolving ability of each formulation is approximately equal to that of 15% HCl.

These acid mixtures provide retardation, with less corrosion at higher temperatures (above 200 °F (93°C)), and have the additional benefit that they will sequester dissolved iron after the acid spends in hot carbonate formations.

Formic acid is also used with HCl for high temperature applications where a slow rate of reaction is required. When extremely high temperatures are encountered mixtures of formic and acetic can be used.

### 10.11 Spearhead Acid Control.

Deeper penetration of acid can also be accomplished by using the technique of "spearhead acid control" (SAC). With this technique, a fracturing fluid is pumped ahead of the acid treatment to achieve the following:

- Generate wider fractures.
- Control leak-off by laying down some sort of filter cake on the fracture faces.
- To cool down the formation.

These actions help to slow down the reaction rate and increase the penetration of the acid treatment.

### 10.12 Gelled Acid.

Gelled Acid is used in fracture treatments of limestone formations. The viscosity serves to retard the acid, reduce friction, reduce fluid loss and provide etching properties. Wider fractures are created using this type of fluid improving the etching pattern. Gelled acid, foamed with nitrogen can generate extremely stable foams and further increase their retarded nature.

An additional, important aspect of Gelled Acid systems is their fines suspending properties. Where “dirty” limestones produce large quantities of fines during acidizing, these can plug the fracture network and reduce the conductivity of the fracture. Using gelled acid systems allows these fines to be produced back from the formation, suspended in the spent acid.

### 10.13 Cross-Linked Acid.

High viscosity cross-linked gelled acid systems have excellent retarding properties for deep penetration into the formation, and are primarily used in the fracture treatment of limestone formations. As with gelled acids, these fluids have excellent leak-off and friction properties, foam forming and fines suspension characteristics.

In addition these fluids can be used to carry proppants for the fracture treatment of sandstone reservoirs. This is particularly useful where the formation is sensitive to water based fluids and low concentration acids are preferred.

### 10.14 Retarded Mud Acid Systems.

Self generating mud acid systems (Retarded Mud-Sol (RMS), SGMA) generate hydrofluoric acid after the acid has entered the formation. The system is pumped from surface with very little hydrofluoric acid present. Once the RMS enters the formation reaction starts, generating hydrofluoric acid allowing deeper penetration of live HF. With this system clays are more effectively removed throughout the zone of acid contact, and a more productive stimulation results. RMS maintains a low pH throughout the contact time thus preventing secondary precipitation.

### 10.15 Sandstone Acid ™.

Sandstone Acid ™ is a unique retarded acid system for sandstone formations. It is a system for moderate to deep penetration which uses conventional HCl:HF acid mixtures with an additional component "HY Acid". This special blend of acids provides powerful retarding properties, unlike conventional HCl:HF mixtures, which react rapidly with clays yielding very shallow acid penetration. The main features of this new acid system are as follows:

- The ability to retard and limit the reaction with clay minerals.
- The ability to increase reaction rates with quartz, thus improving overall permeability.

These features allow the use of stronger acids than would be used in conventional systems, particularly where the formation contains large amounts of clays. Thus strong acids can be placed deep into the formation without risk of de-consolidation of the near wellbore region. In addition, the application of this acid can be extended to it's use in acid fracturing low permeability (2.0 to 10 md) sandstone formations.

### 10.16 Acid Strength.

The strength of acid used is dependent on the solubility of the formation, with some basis placed on previous experience in a given area and common sense. (Refer to Table 14, page 67)

If the formation has less than 10% solubility 3.0% to 15% hydrochloric acid is used. Stronger hydrochloric acid strengths (15% to 28%) are used to obtain more live acid further from the wellbore for deeper penetration. Where organic or mixed acids are used, strengths equivalent to the dissolving power of hydrochloric acid are used.

**Table 18: Relative Retarding Action of Different Systems.**

| **Regular Acid** | **Mixture of HCl + Organic** | **Chemically Retarded Acid** | **Physically Retarded Acid** |
|---|---|---|---|
| **Least** | → **Retardation** → | | **Most** |
| HCl Acid | Super-Sol (EQH) Acids | Sta-Live Acid Systems | Gelled Acids and Crosslinked Acid. SRA-3 Emulsified Acid |
| HCl:HF | | Retarded Mud Sol Systems. (HCl:HF) SGMA | Sandstone Acid ™ |

## 11. Applications of Nitrogen In Acidizing.

- Atomized Acid.
- Nitrified Acid.
- Foamed Acid.

### 11.1 Atomised Acid.

Inject fluid as fine mist of droplets in gas phase:

- Where water blocks are present or are likely to occur during acidizing.
- Better removal due to higher mobility of gas.
- High velocity of expanding gas aids clean-up of fines etc. from the producing formation.
- High penetration of acid into smaller rock crevices and fractures.
- Increased coverage due to expanded acid volume.

Gas to liquid ratios.

- Use the correct amount of acid to remove all soluble material.
- Near well-bore blockages:

  1:1 or 2:1 should be used (Nitrogen to Liquid).

- Larger areal coverage with given volume of acid:

  4:1 to 6:1 should be used.

- Amount of nitrogen used is dependent on:

  Bottom hole pressure.
  Bottom hole temperature.
  Calculated expansion ratio.

### 11.2 Nitrified Acid.

- Effective and economic due to alleviation of need to swab.
- Due to its low solubility, nitrogen assumes state of compressed gas bubbles. Acts as source of energy inside injected fluids.
- Flow back, expansion of bubbles forces fluids towards well-bore and up to surface. Aids removal of formation fines etc.
- Additional volume due to gas, increases radial penetration for given acid volume.
- Volume of nitrogen in fluid needs to be calculated to determine correct volume of flush to be pumped.
- Each job must be designed individually.
- Use tables to determine ratio of gas to liquid based on well conditions.

## 11.3 Foamed acid

- Foam is a gas in water emulsion using ± 1.0% surfactant as emulsifier.
- Stable, low fluid loss foams at bottom hole conditions are formed using 52 - 95% gas volume with a continuous aqueous fluid phase.
- Acid recovery is a problem in low pressure reservoirs. Foam gives immediate acid clean-up and eliminates swabbing
- Foam eliminates need for extensive acid reaction rate retardation
- Foam aids removal of formation fines etc.

### 11.3.1 Nitrogen Retention.

- Nitrified acid usually contains 500 to 1000 scf/bbl of nitrogen.
- Nitrogen reduces hydrostatic head of acid, and allows natural flow.
- Nitrogen may separate from acid in formation. In this case low pressure wells may require swabbing.
- Use of up to 1.0% foaming agent allows retention and dispersion of nitrogen throughout acid.
- As the acid spends, gas in fluid emulsion remains intact.
- Gas provides energy to lift the spent acid.

### 11.3.2 Foamed Acid Diverting.

- In large formations, acid will tend to enter most permeable or lowest pressure zone.
- Foamed acid can divert the treatment from one set of perforations to another.
- Foam viscosity can be very high (depends on shear rate).
- Increasing the fluid viscosity by use of foam pads between acid stages will divert the acid to new intervals by increased pressure.
- If all the acid is foamed prior to pumping it will have inherent diverting properties.

### 11.3.3 Foamed Acid Applications.

Any well requiring acid stimulation is a candidate for foamed acid or staged nitrified and foamed acid treatments.

- High pump rates are not required and can be undesirable.

- <u>Matrix treatments:</u>

  |Use 60 to 70% quality foam

- Foamed acid fracturing:

  Use 70 to 80% quality foam

Normally foamed acid is preceded by a nitrified acid spearhead to achieve better penetration. After initial penetration of low viscosity nitrified acid, foamed acid is pumped at 65% to 80% quality. This procedure provides:

- Deeper penetration due to low fluid loss.
- Good diversion due to increased viscosity.

In low API gravity oil wells.

- Spearhead with solvents (xylene or toluene) to remove any heavy deposits (asphaltenes or paraffins), and allow the acid to react with the formation face.
- Allow the solvent to soak for several hours (4 hours) before commencement of the acid treatment.

Wells with scale problems.

- Fill tubing or casing with foamed acid over-flush with 10.0 bbl.
- Shut in well for controlled reaction time.
- Flow back well at highest rate possible.
- If no corrosion test data:

  Inhibit acid for 4 hours at BHT
  Unload well after 3 hours shut-in.

### 11.3.4 Lower Quality Foamed Acid.

- Foam qualities below 55% :

  Do not have stable characteristics.
  Viscosity desirable for better conductivity than with conventional acids.

- Applications in deep wells:

  Used to lower the hydrostatic head.
  35 to 55% quality foamed acid is a more efficient fluid with respect to leak-off than gelled and emulsified acids, or acid containing other fluid loss control agents

## 12. Viscosity and Friction Pressure.

### 12.1 Viscosity.

Since acids systems have a water base, their viscosity is about 1.0 centipoise and they behave as Newtonian fluids with easily predicted flow properties. However, when they are altered by adding gelling agents or polymers, or when combined with hydrocarbons to form emulsions, they become Non-Newtonian and more complex in behaviour. Generally, low viscosity Newtonian acids are used in matrix acidizing, whilst viscous Non-Newtonian treating solutions are used when acidizing within natural fractures and in fracture acidizing.

Viscosity is defined as the property of a fluid that resists the force tending to cause the fluid to flow. The common oil field unit of measure for viscosity is the centipoise (cp), which is expressed in centimetre-gram-seconds.

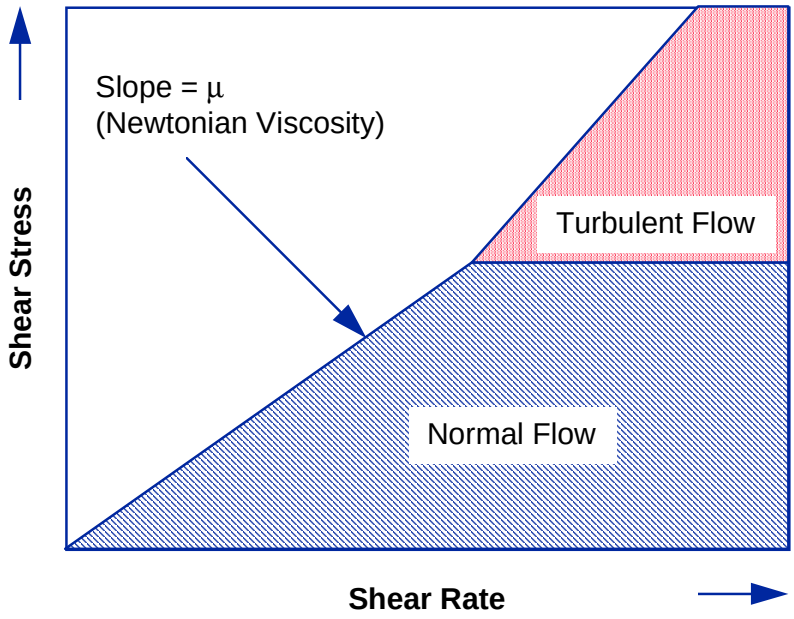
### 12.2 Newtonian Fluids.

A fluid undergoes continuous deformation when subjected to a shear stress, such as when it is pumped. Some fluids follow a standard pattern of behaviour under shear stress (i.e. when subjected to pump pressure). Specifically this standard pattern is that shear stress is directly proportional to the rate of shear (Figure 16).

A fluid which behaves in this manner is classified as a Newtonian fluid and its flow properties can easily be predicted from a measurement of the fluids viscosity. Viscosity is the single rheological property needed for the flow calculations of a Newtonian fluid.

Common examples of Newtonian fluids are water, most oils and most other liquids that do not contain solid particles in suspension.

**Figure 16: Typical Newtonian Fluid Profile**.




| | | | | |
|---|---|---|---|---|
| Shear Stress | = | m x (Shear Rate) | | |
| m | = | μ | | |
| μ | = | Shear Stress / Shear Rate | = | Coefficient of Viscosity |

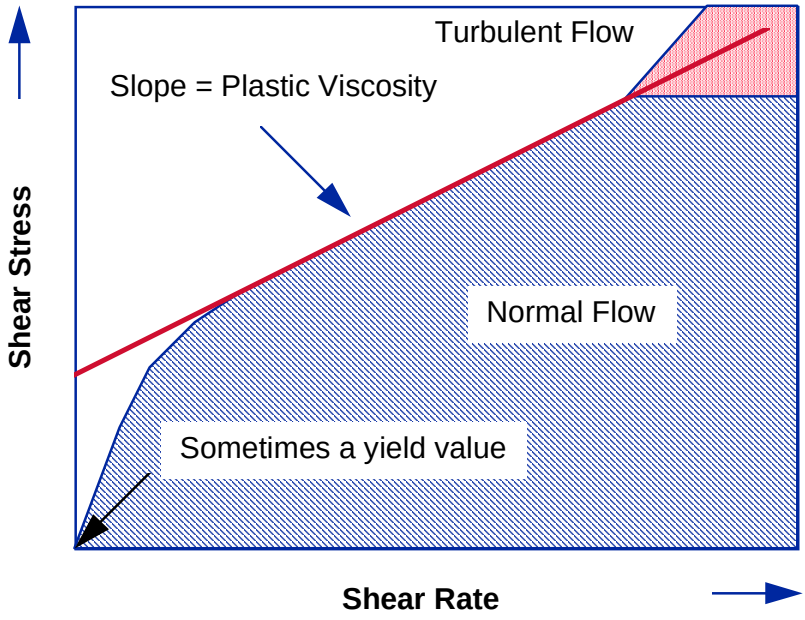
| | | | |
|---|---|---|---|
| Analogy: | Shear Stress | ≡ | Pressure |
| | Shear Rate | ≡ | Pump Rate |

## 12.3 Non-Newtonian Fluids.

In some specialised acid treating solutions, flow properties are changed by adding synthetic or natural polymers, or by combining the acid with a hydrocarbon such as kerosene to form a viscous emulsion (as in BJ Services Emulsified Acid or SRA-3 acid).

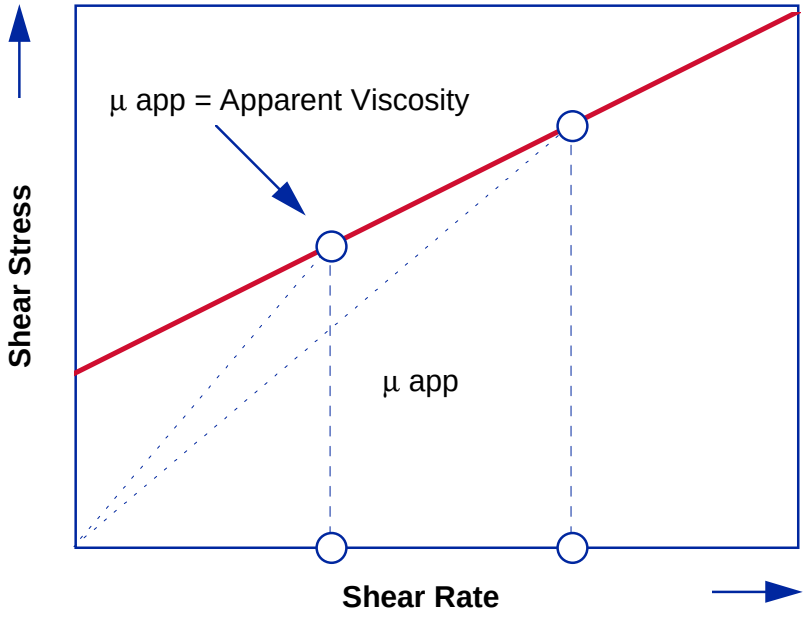
These fluids are Non-Newtonian which may be defined as materials which do not conform to direct proportionality between shear stress and shear rate (Figure 17) Consequently, Non-Newtonian fluids do not exhibit a simple viscosity and their consistency changes as their flow rate changes. In acid stimulation, flow rate is related to pumping rate, pipe size, size and number of perforations and other factors.

**Figure 17: Typical Non-Newtonian Fluid Profile.**




In general, Non-Newtonian fluids become less "viscous" at higher pump rates (shear thinning) and are often unstable at these rates (turbulence). In effect the apparent viscosity of the fluid becomes less as it is pumped faster (Figure 18).

**Figure 18: Apparent Viscosity.**




Where Apparent viscosity (μ app) = Slope of the line at a given shear rate.

The effects of viscosity must be considered when designing acid treatments. In matrix acidizing, where injection rates are low, the viscosity of the treating solution should be kept to a minimum to prevent excessive pressures during placement and to aid in the clean-up of the treatment when the job is complete.

On the other hand , a viscous acid has advantages when stimulating within natural fractures or when fracture acidizing for deeper penetration. In these treatments the higher viscosity helps to control fluid leak-off, increasing the efficiency of the acid as a fracturing fluid.

**Figure19: Viscosity of Hydrochloric Acid versus Concentration.**

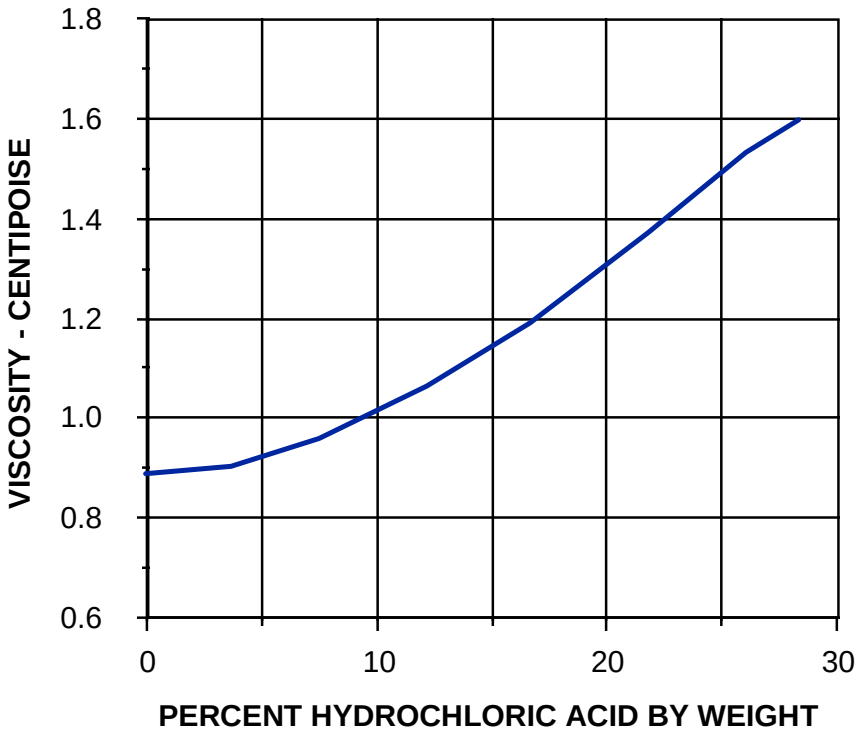
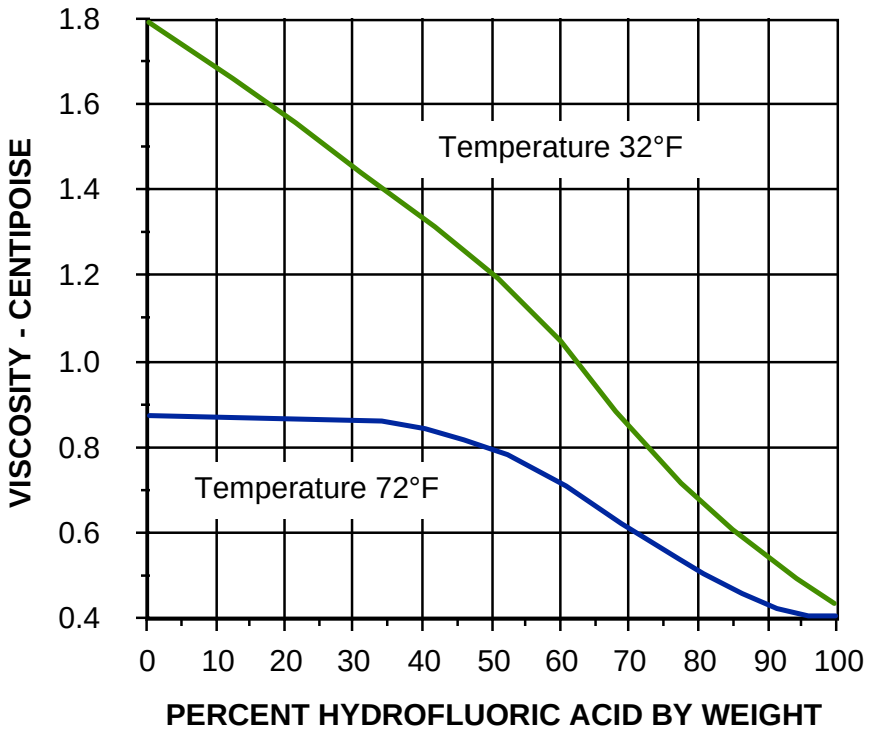


**Figure 20: Viscosity of Hydrofluoric Acid Versus Concentration.**




**Note:** This Graph is for Raw Hydrofluoric Acid, which for reasons of safety is not in common use.

## 12.4 Friction Pressure.

For the successful design of well stimulation treatments, it is necessary to know the amount of friction pressure that will be encountered when pumping the fluids through tubular goods or through the annulus between tubing and casing.Friction Pressure may be defined as:

> "The pressure (or head) lost by flowing water or other fluids, as a result of friction between the moving fluid and the walls of the conduit."

A simpler definition might be :

> "Pumping energy lost because of fluid drag in the pipe."

The friction pressure of unaltered, aqueous based acid (as with its viscosity), is very nearly that of water. To correct for the deviation that does exist when calculating acidizing treatments, a factor equal to the specific gravity of the acid is used in the friction pressure equation.

Friction pressure values for water can be found by the use of Figure 22 through to Figure.

Friction Pressure of Acid =

Specific Gravity of Acid x Friction Pressure of Water. (Equation 1)

When high pumping rates are required, friction reducing agents can be used to reduce the friction pressure of aqueous acid solutions pumped through tubular goods by as much as 60%. Where acids have been emulsified with a hydrocarbon, the friction pressure losses may be more than double that for regular acid. For this reason, pumping rates are usually kept low when using emulsified acid systems.

## 12.5 Friction Reducing Agents.

Expressed in the simplest terms, friction reducing agents work by minimising the amount of turbulence in fluids flowing through tubular goods. All friction reducers in use today are long-chain natural or synthetic polymers. When the polymers are dry, they can be considered as resembling tightly coiled springs. When water is added, the springs uncoil. Thus polymers in solution serve as a multitude of elastic "layers" that suppress turbulence.

In classifying friction reducers, the most obvious divisions are by base fluid. The two base fluids involved in well stimulation are hydrocarbons (kerosene, diesel and crude oils), and aqueous fluids (water, brine and hydrochloric acid).
Agents used to reduce friction in hydrocarbons are synthetic polymers and "in situ" soap gels, whilst the agents for aqueous systems are guar (natural gums) and synthetic polymers.

However, additives that can be used as friction reducers in acid solutions are few in number. Many natural polymers (such as guar) that are efficient in water and brine systems, become totally ineffective in acid. Chemical reaction with the acid breaks the polymer into shorter chains or into monomers. When this occurs the polymer no longer has the ability to suppress turbulent flow and high friction pressure results. High molecular weight non-ionic polymers are the most commonly used friction reducers for acid. These chemicals resist attack by acid at normal treating temperatures.

Figures showing friction pressure for water can be used when friction reducing additives are employed for use with freshwater, acid, or brine. This is accomplished by using the a relative friction factor R.

To determine the friction pressure when an additive is used, determine the friction pressure for the base fluid (Equation 1), pumped at the desired injection rate, and multiply this number by the R factor corresponding to the type and amount of friction reducer used.

Tables and graphs for these factors can be found in the BJ Services Mixing Manual and in the product technical brochures for these additives. In some cases the friction factor R is expressed as a percentage of friction reduction which can be expressed as decimal and used in this equation. The equation to apply is as follows:

Equation 2.

Total Friction Pressure =

$$\frac{\text{(Friction Pressure for water)}}{1000\ \text{ft}} \times \text{Length of pipe} \times \text{Specific Gravity} \times R$$

**Note:** This method should not be used for emulsified acids or other Non-Newtonian fluids (Cross-linked Acid).
It is relatively easy to calculate the friction pressure of Newtonian fluids such as water, water based acids, and API oils from basic rheological data. However, gelled and crosslinked fluids used in fracture acidizing are Non-Newtonian and their friction pressure is much more difficult to calculate (where, possible published experimental data can be used). To aid with this many computer programs are available using various models that calculate the flow properties of these fluids based on rheological data.

It should be noted that, translation of laboratory generated data for use in the field is not extremely accurate. This is because variables in the laboratory can be more closely controlled, particularly relating to friction reducing systems and the tubular goods through which they are transported.

Variance in parameters such as pipe roughness, base fluid properties, temperature (ambient and downhole), and mixing procedures, are some of the variables that often lead to differences between calculated data and actual field performance.

Since these variations exist, and are largely unavoidable, information from experimental data should be considered as reasonable estimates rather than absolute values. To reduce this margin of error laboratory procedures should try to simulate field conditions as closely as possible, and scale-up from laboratory to field should be conservative.

## 12.6 Flow Patterns.

The mechanics of friction reduction can be better understood by examining the changes in the flow patterns shown by fluids at various flow rates as illustrated in Figure 16.

The left hand illustration (a) shows Laminar flow where flow direction is in a line parallel with the wall of the pipe, with little loss of pump energy. This is typical of low pump rate conditions such as in matrix acidizing.

During most acidizing and fracture treatments, the fluids are flowing too fast to be in Laminar flow. The centre illustration (b) depicts Turbulent flow. Fluid in a violent swirling motion occupies essentially the entire area of the pipe. More fluid is transmitted through the pipe but energy losses due to the random turbulent pattern are high. Therefore friction pressures are high.

The right hand illustration (c) shows the same stream after a friction reducer has been added. Notice that the turbulence has been dampened and reduced. More pump energy is now directed to increasing fluid velocity rather than overcoming fluid drag.

**Figure 16: Types of Fluid Flow.**

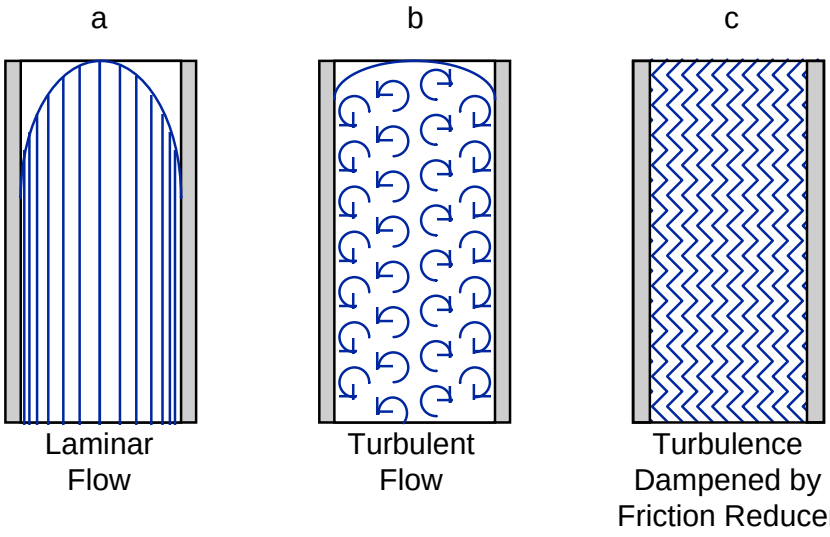


**Figure 22: Friction Pressure of Fresh Water Pumped Through Various Tubing Sizes.**

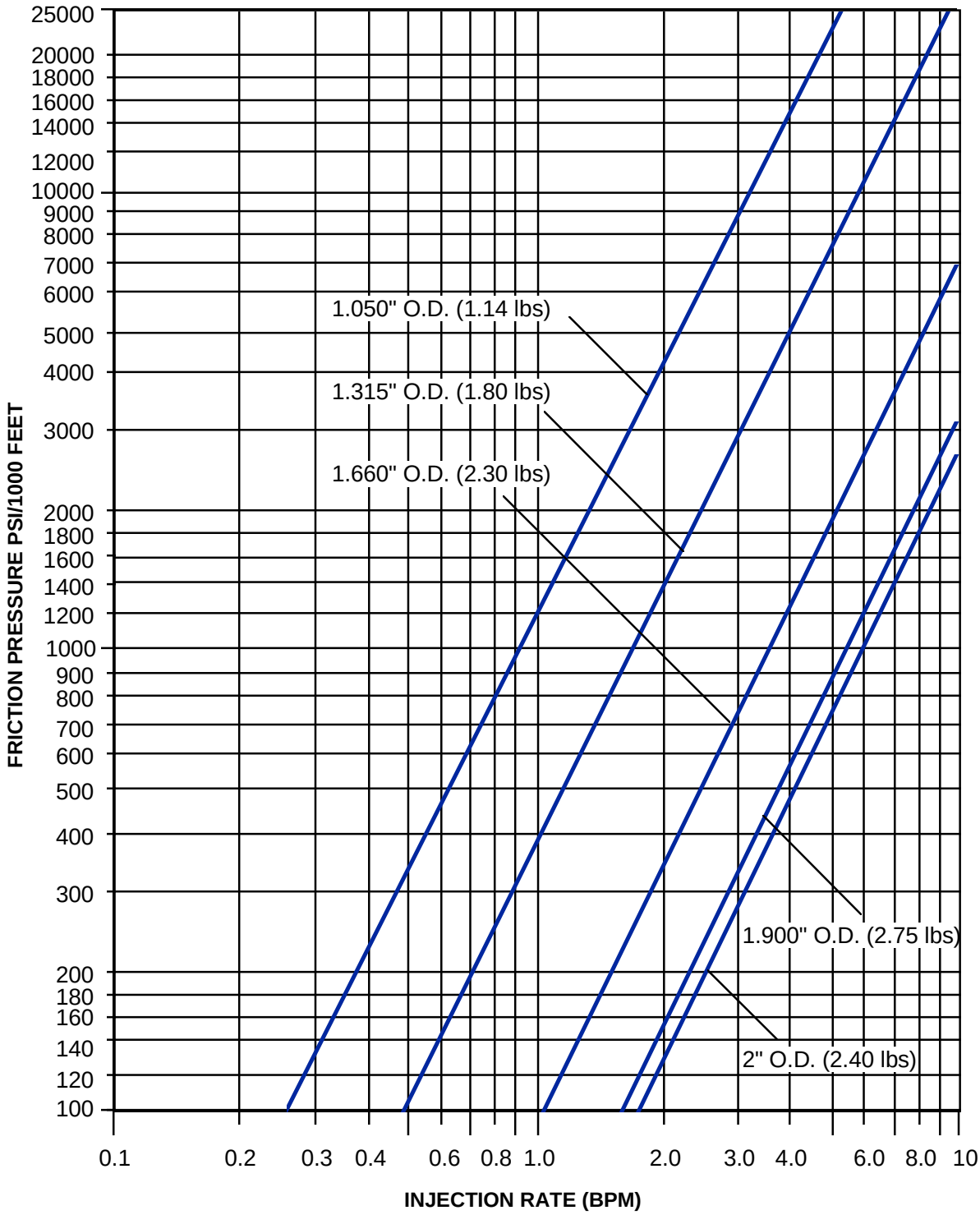


**Figure 17: Friction Pressure of Fresh Water Pumped Through Various Tubing Sizes.**

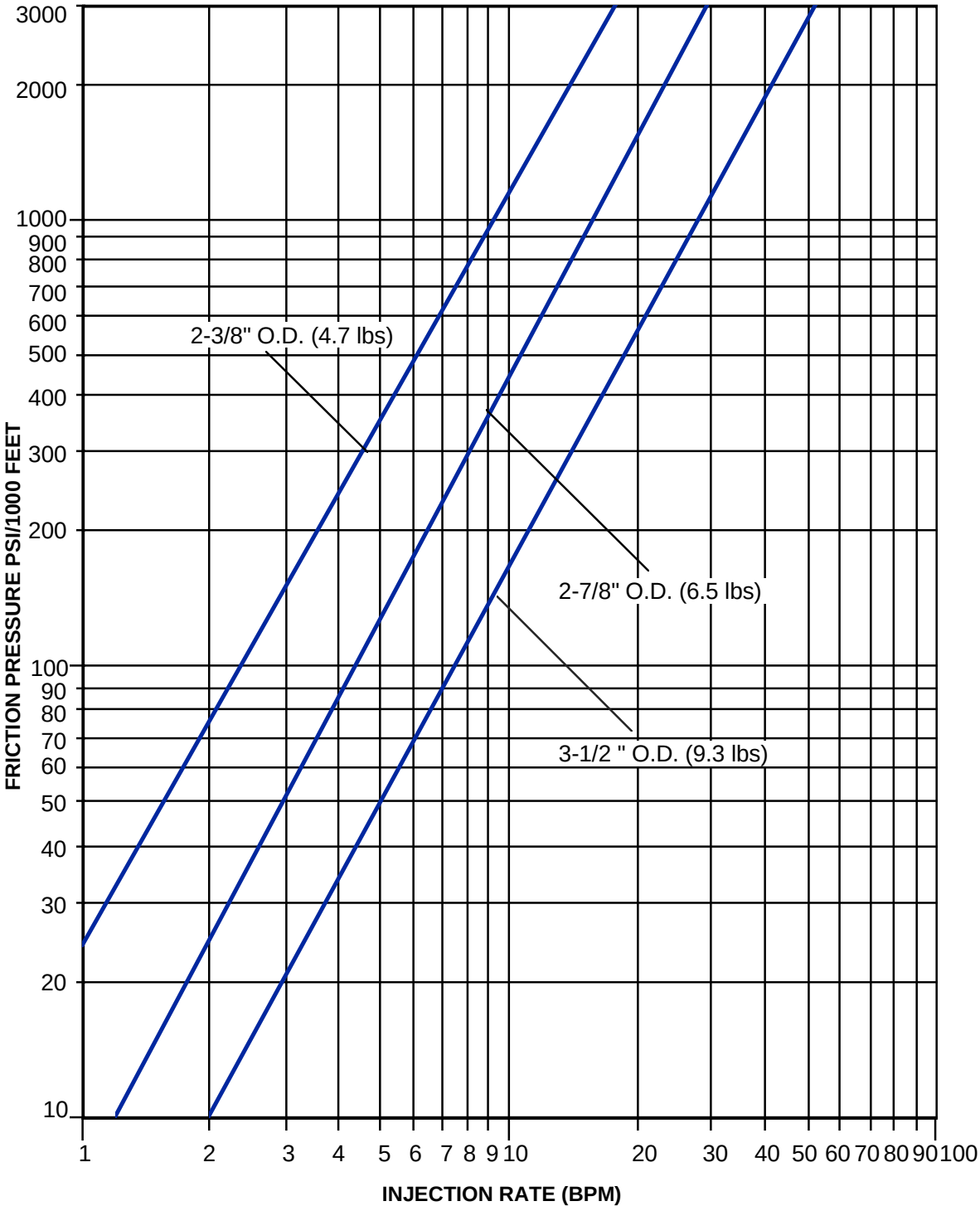


**Figure 18: Friction Pressure of Fresh Water Pumped Through Various Casing Sizes.**

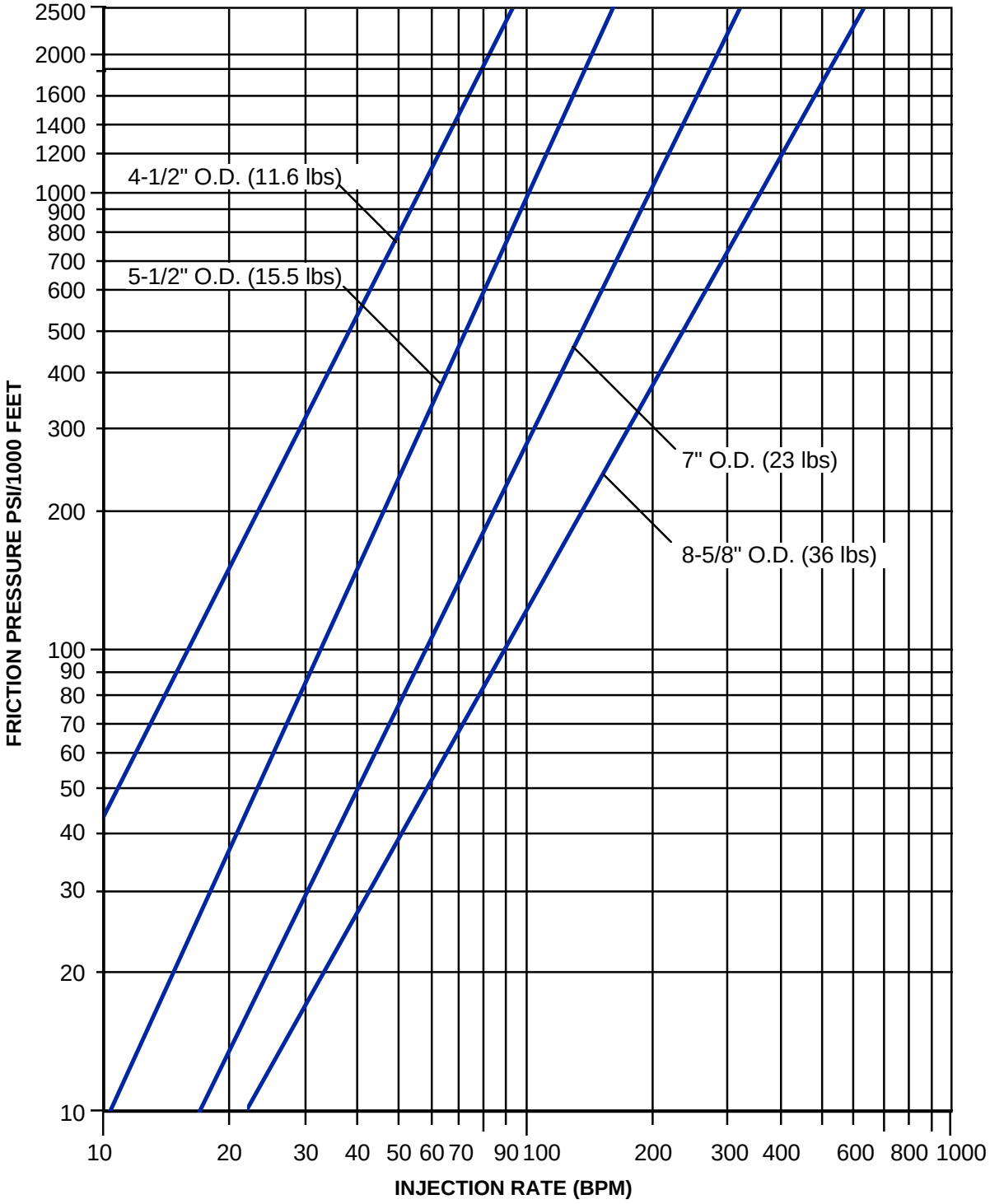


**Figure 19: Friction Pressure of Fresh Water Pumped Through the Annulus Between 4-1/2 Inch Casing and Various Tubing Sizes.**

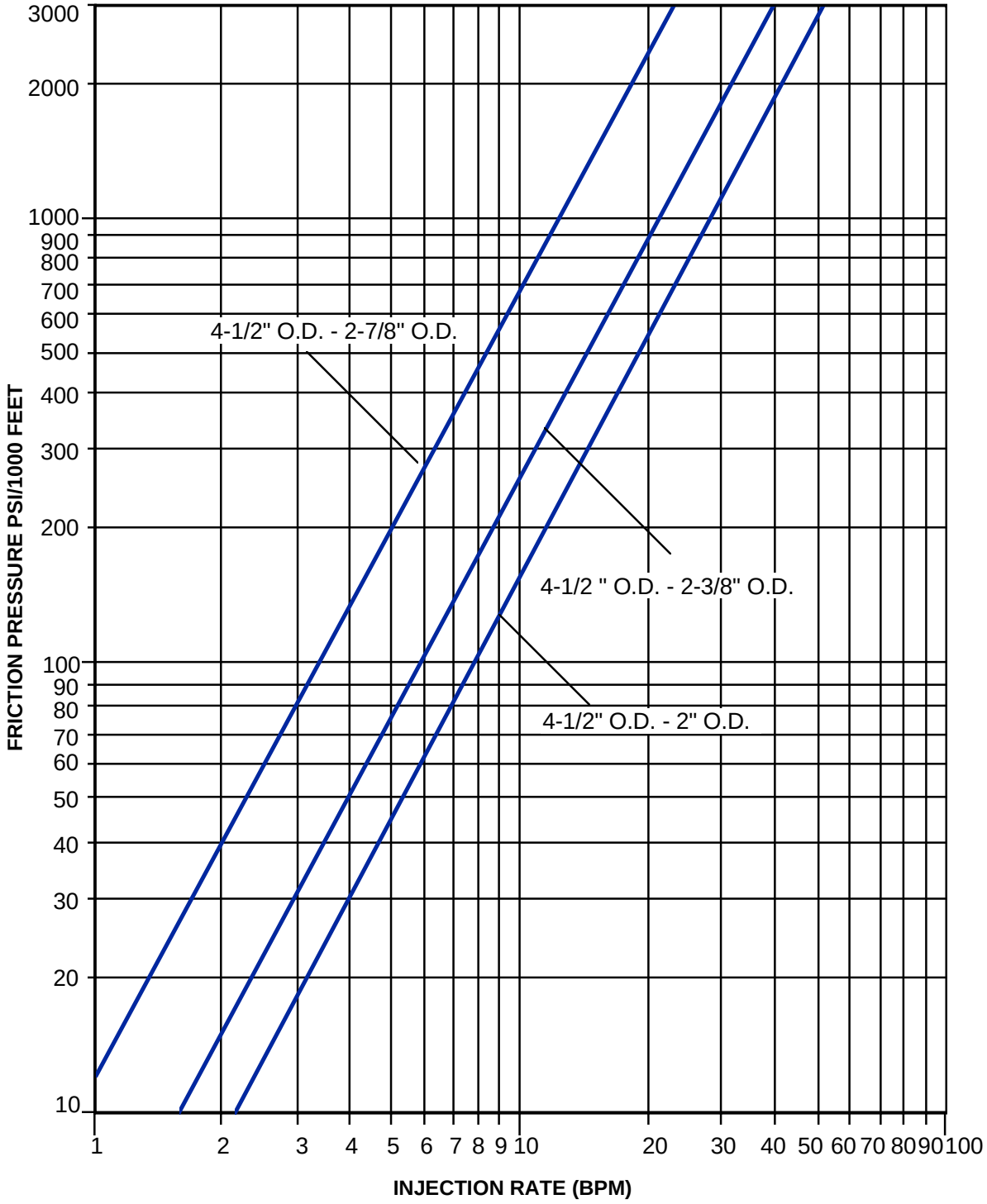


**Figure 20: Friction Pressure of Fresh Water Pumped Through the Annulus Between 5-1/2 Inch Casing and Various Tubing Sizes.**

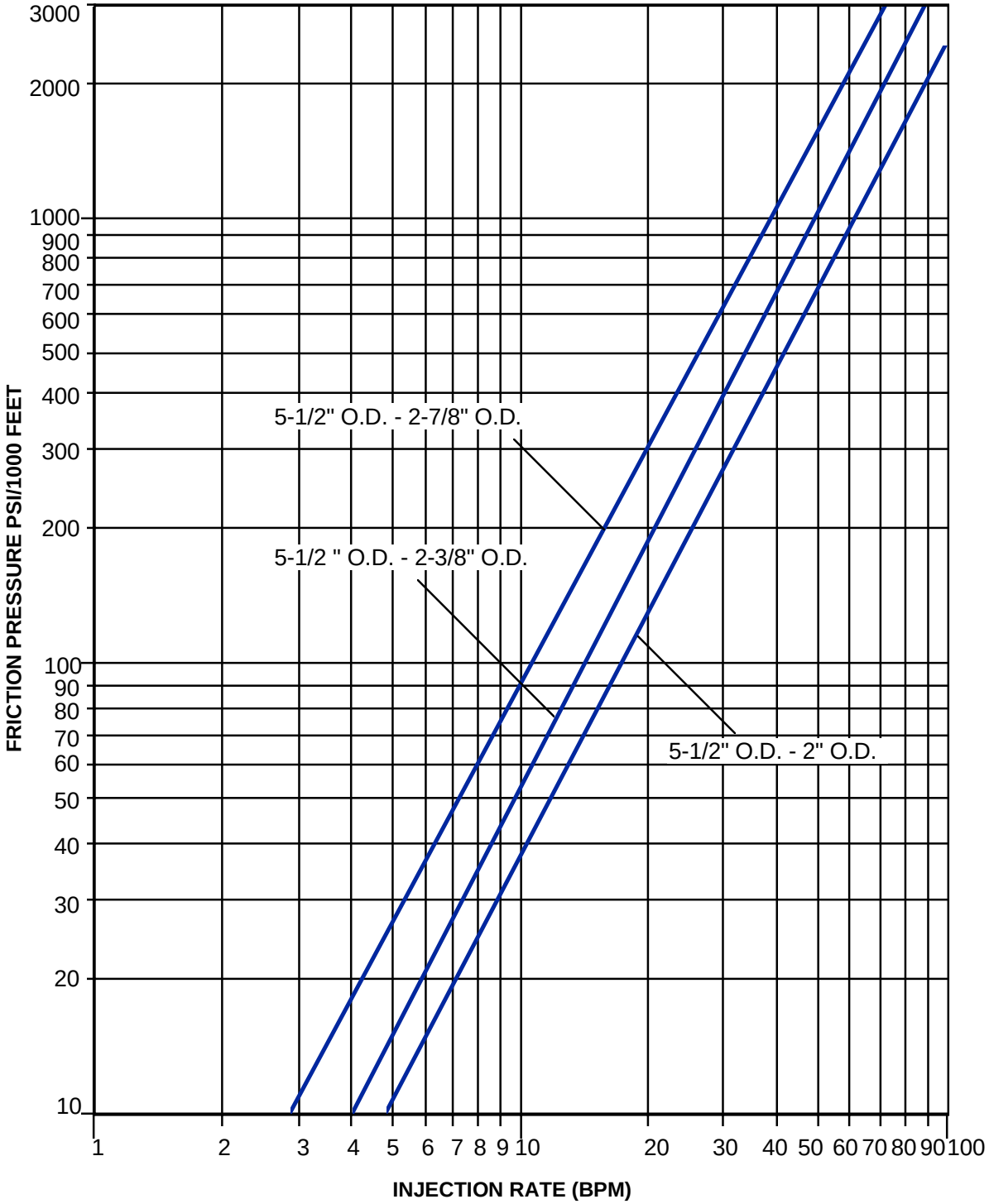
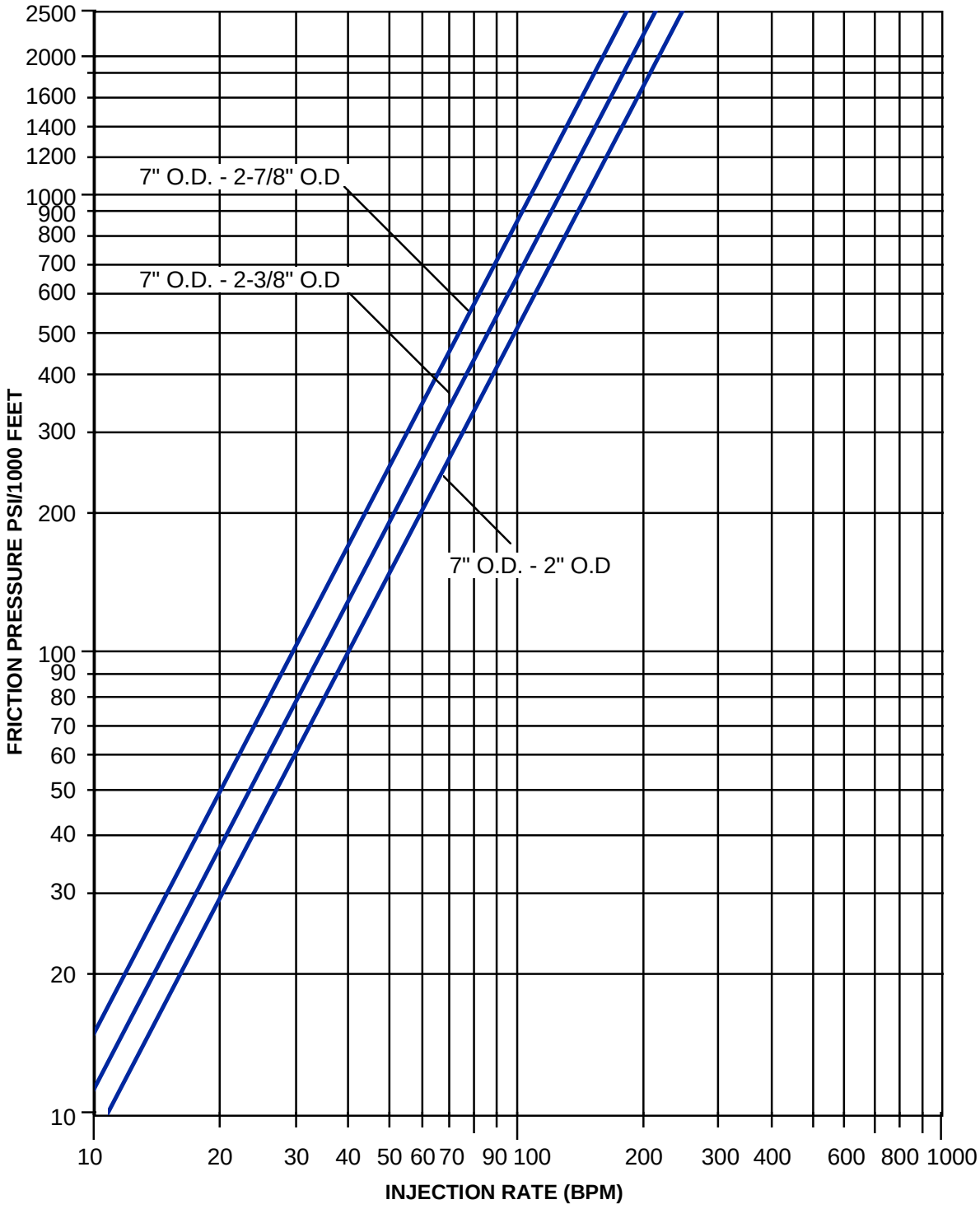


**Figure 27: Friction Pressure of Fresh Water Pumped Through the Annulus Between 7 Inch Casing and Various Tubing Sizes.**



## 13. Job Design Considerations.

### 13.1 Spotting Fluids in the Wellbore.

Special down hole problems may make it necessary to completely immerse a specific area of the wellbore with acid, for example:

- Removing permeability damage caused by mud filter cake or scale deposits on the formation face or in perforation tunnels.
- Freeing stuck pipe.
- Dissolving junk in the hole.

When spotting acid in the annulus to solve these problems, the fluid columns in the tubing and in the casing must be either balanced so that no pressure differential exists, or enough pressure must be held at the surface to balance out the difference in hydrostatic heads.

#### 13.1.1 Balanced Columns Method.

When it is necessary to balance the fluid columns, the height to be filled with acid and or solvent must be determined and the volume of fluid calculated. When this volume has been pumped into the well, just enough flush and displacement fluid should be pumped to balance the fluid columns, that is, that the top of the acid and or solvent is at the same level both inside and outside the treating string (if the hole is standing full).

#### 13.1.2 Unbalanced Columns Method.

When the bottom of the tubing is below the treating area, enough flush and displacement fluid must be pumped to displace the acid down the tubing and up the annulus to the desired location. Normally this spotting method results in an unbalanced condition between the volumes in the tubing and casing. To prevent further fluid movement towards equalisation enough pressure must be held on the tubing at surface to balance out the difference in hydrostatic heads.

Relatively small volumes of fluid are used in spotting pickling and solvent soak treatments (250 to 1000 gallons). The precise volume used depends upon the nature of the treatment and the length of section to be filled.

Acid treating solutions typically employed in pickling treatments are NE-Type Acids which normally consist of inhibited hydrochloric acid with the necessary demulsifying and low surface tension surfactants. Other acid systems used include Mud Sol acids, Clean-up and MMR acids, One Shot acid, Sequestering, Organic acids and

Organic hydrochloric acid blends. Gelled acids and retarded acids are not normally used for these types of operations.

## 13.2 Pressure Design Considerations.

1. When matrix acidizing, the bottom hole fracture pressure (BHFP) must not be exceeded. (The fracture pressure decreases with reservoir pressure). BHFP and surface treating pressure (STP) should be determined. All personnel involved, should be informed of the maximum STP and instructed not to exceed it.

2. Injection rate control should be maintained for low reservoir pressure by using nitrogen or a control valve.

3. If the treatment is done over balanced, solid diverting materials such as Oil Soluble Resins (OSR) or Benzoic Acid should be used. Uniform zonal coverage is difficult to achieve when overbalanced. Overbalance causes the highest incidence of unplanned fracturing.

4. If the treatment is performed under-balanced, non particulate diverting material can be effective. Utilisation of Nitrogen in conjunction with foam or solids is required. 100 % equipment back-up should be utilised.

Treatment guidelines for sandstone reservoirs with Nitrogen and Carbon Dioxide:

**Table 19: Carbon Dioxide ($CO_2$) and Nitrogen ($N_2$) Guidelines.**

| Reservoir Type | Nitrogen | Carbon Dioxide |
|---|---|---|
| Gas. | Yes | Yes (1) |
| Low Pressure Gas. | Yes | (2) |
| Oil, (Above the Bubble Point). | (3, 4) | Yes |
| Oil, (Below the Bubble Point). | Yes | Yes |
| Water Injection or Disposal Well. | (3, 4) | (3, 4) |

1) Larger volumes are normally required to create a free gas phase.
2) Due to higher $CO_2$ density, sufficient pressure may not be generated to achieve back flow.
3) Temporary trapped gas saturation may affect penetration and recovery.
4) Technical staff approval required.

## 13.3 Injection Rate and Surface Treating Pressure.

The injection rate of an acid treatment can greatly influence the placement of the acid and therefore the success of the treatment. The type of acidizing job (matrix, natural fractures or fracture acidizing) usually determines the ideal injection rate.

### 13.3.1 Low Injection Rates.

Pump rates which produce pressures below that required to fracture a formation, usually place the acid in the near wellbore area, within the rock matrix and where present, in naturally occurring fractures. Low rates are recommended to repair skin damage, shallow damage or where it is not intended to fracture the formation, as when treating in proximity to a zone of high water saturation.

Practical factors that influence the rate used, and which require that the rate is kept low are:

- High formation pressures.
- Pressure limitations of the tubular goods.
- Pressure limitations of other well equipment.

### 13.3.2 High injection Rates.

Due to the high reaction rates of hydrochloric acid with carbonates present in the formation, higher injection rates are required for deeper penetration of live acid. Since high injection rates customarily involve high pressures, the formation is likely to be fractured during such treatments.

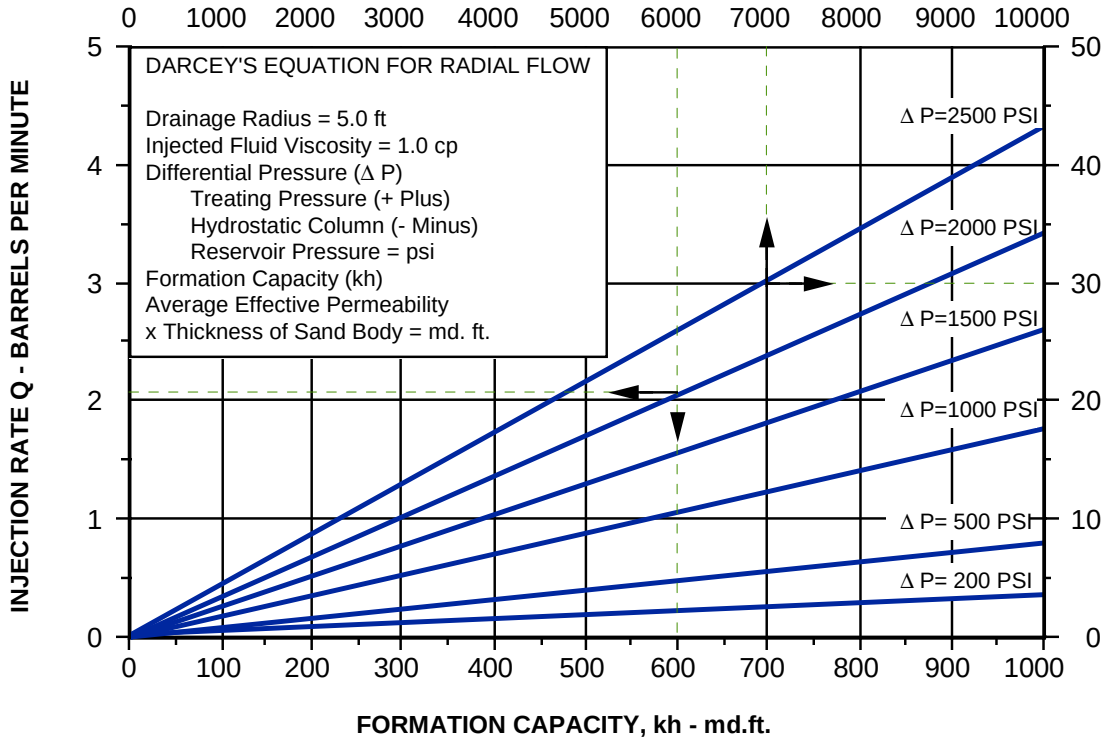
On multi-zone treatments, where several zones accept fluid at different pressures, more complete coverage can be obtained by employing a high rate of injection. (Limited entry techniques).

## 13.4 Establishing Pump Rate and Surface Treating Pressure.

Sandstone matrix stimulation treatments are performed at less than fracturing pressures. If the formation is fractured, the stimulation fluid takes the path of least flow resistance through the fractures and does not uniformly contact the desired treating interval. This results in uneven drainage of the reservoir and only slight increase in the productivity.

Figure 21 is used to establish the maximum allowable pump rate that will not fracture the reservoir.

**Figure 21: Injection Rates (Non-Fracturing) into Permeable Formations at Various Differential Pressures.**




( For small volume treatments in partially saturated reservoirs)

The maximum surface treating pressure at the maximum allowable pump rate is calculated as follows:

Maximum Surface Treating Pressure =

(Fracture Gradient x TVD) + Friction Pressure - Hydrostatic - 300 psi

Note : 300 psi is an arbitrary safety factor to assure that the reservoir will not be fractured.

In many sandstone matrix stimulation treatments, the initial injection rates will be substantially less than those predicted when using the above equation and Figure 21, when pumping at the maximum allowable treating pressure. This is caused by permeability damage in the near wellbore area. Once this damage is removed by the acid , the predicted and actual injection rates will be close in value.

When the calculated injection rates are less than 0.5 barrels per minute, the well probably will respond better to a proppant fracturing treatment, than to a sandstone matrix treatment, since the treating time would be extremely long for matrix stimulation.

Example :

| | | |
|---|---|---|
| Well Depth (TVD) | 9500 | ft |
| Permeability | 100 | md |
| Formation Thickness (MD) | 10 | feet |
| Fracture Gradient | 0.65 | psi/foot |
| Fluid in Hole | 15%:4.0% | HCl:HF |
| Hydrostatic Pressure Gradient | 0.476 | psi/foot |
| Formation Pore Pressure | 4500 | psi |
| Tubing Size | 2-3/8 | inch |

Formation Fracture Pressure = Fracture Gradient x Depth (TVD)
= 0.65 x 9500
= 6170 psi

Hydrostatic Pressure = Hyd. Pressure Gradient x Depth (T.V.D.)
= 0.476 x 9500
= 4522 psi

Differential Pressure = (Formation Fracture Pressure) - Formation Pore Pressure - 300 psi
= 6170 - 4500 - 300
= 1370 psi ($\Delta P$)

Formation Flow Capacity = Formation Thickness (MD) x Permeability
= 10 x 100
= 1000 md. ft.

Maximum Injection Rate (From Figure 21) = 2.3 Barrels Per Minute.

Friction Pressure (From = Friction Pressure From Figures x

Figure **17**, page 100) Specific Gravity x Depth (MD)/1000
= 90 x 1.08 x 9500/1000
= 922 psi.

Surface Treating Pressure = (Fracture Gradient x TVD) + Friction Pressure - Hydrostatic - 300 psi

= 6170 + 922 - 4522 -300 psi
= 2270 psi

Therefore maximum surface treating pressure is 2270 psi at a maximum treating rate of 2.3 barrels per minute.

### 13.5 Shut-In Times.

Shut-in time is the length of time a well is closed in after a stimulation treatment is completed, before flow back is initiated. This time is determined by the type of acid used and by downhole factors such as formation type, bottom hole temperature and bottom hole pressure.

After an acid solution has been neutralised by reaction with the formation, it is no longer a stimulation fluid. However it may become harmful to the formation permeability if allowed to remain downhole.

#### 13.5.1 Hydrochloric Acid with Limestone.

Hydrochloric acid reacts so rapidly with limestone that it is essentially neutralised by the time the acid has been completely placed. This generally holds true at all ranges of temperature and pressure. Since limestone formations incorporate varying amounts of insoluble materials that can plug permeability, if allowed to come to rest, it is important to remove the neutralised hydrochloric acid as soon as it is spent. Shut-in times with such formations is zero.

#### 13.5.2 Retarded or Emulsified Acid.

When chemically retarded acids such as the Sta-Live systems, and emulsified acids such as SRA-3 are used, the reaction time of the acid can exceed the displacement time. Here a shut-in time of one to two hours is recommended for maximum stimulation. The shut-in time may be extended where there is sufficient bottom hole pressure to promote rapid clean-up.

#### 13.5.3 Organic Acid and HCl Acid Mixtures.

Mixtures of acetic or formic acid with hydrochloric acid delay the time required for complete spending of the acid mixture and thus require a shut-in time.

#### 13.5.4 Gelled and Cross-Linked Acid Systems.

When Gelled or Cross-linked acids are used the reaction time of the acid can exceed the displacement time. In these cases, longer shut-in times are required to allow time for the acid to fully spend and the viscosity to be reduced to allow easy flow-back.

### 13.5.5 Sandstone Acidizing with HCl: HF Mixtures.

The acid mixtures required to stimulate sandstone reservoirs sometimes create special problems. For example, the reaction rate of hydrofluoric acid with sand, clay and silt is much slower than the practical injection rate. But because of detrimental side effects such as the formation of $Na_3SiO_6$, $CaF_2$, and NaF, the shut-in time should be limited to the time required to prepare the well to flow back.

Other harmful effects can result from excessive shut-in times with sandstone reservoirs. One such effect is the reaction of acid solutions with water sensitive clays. While acid is not believed to swell these clays, its reaction does dislodge portions of the clay that can act to block the flow of fluids into or out of the well.

Another potentially harmful effect stems from the reaction of hydrochloric acid on the soluble carbonate material that consolidates the sand grains in most sandstone formations. Reaction with hydrochloric acid can remove this consolidating material, breaking down bonds between the sand grains. The result can be an unconsolidated sand zone with a lowered permeability. To avoid this problem careful attention should be paid to the strength of hydrochloric acid selected based on temperature and carbonate content of the formation.

Where excessive shut-in times cannot be avoided, such as when sucker rods or downhole pumps have to be run to flow back the well, it is advisable to overflush the acid treatment with brine or water, a sufficient distance out in to the formation, to prevent deposition of undesirable reaction by-products in the near wellbore area.

## 14. Acid Fracturing Concepts and Design.

### 14.1 Introduction to Hydraulic Fracturing.

Hydraulic fracturing is a process of creating a fracture by the injection of fluids into a formation at a pressure higher than the parting pressure of the formation. Injection rate has to be high enough and formation permeability to the injected fluid has to be low enough that fluid loss is not excessive in which pressure can build up and sufficient to fracture the formation or to open existing natural fractures.

Normally, proppants are injected with fluids to prop the fracture open in sandstone formations, and acids are used to etch the fracture faces making them uneven to prevent them from completely closing in carbonate formations. The propped or etched fracture will act as high conductivity passage for fluids to move to the wellbore with much ease.

Hydraulic fracturing has been used to accomplish four basic jobs:

1. Overcome wellbore damage (high permeability formations).
2. Create deep-penetrating fracture into reservoir to improve the productivity or injectivity of a well.
3. Aid in secondary recovery operation.
4. Assist in the injection or disposal of brine and industrial waste material.

| Acid Fracturing | Propped Fracturing |
|---|---|
| • Carbonate (limestone, dolomite). | • Sandstone. |
| • Acid for etching. | • Proppants. |
| • Excessive fluid loss. | • Controlled fluid loss. |
| • Short etched half-length. | • Long propped half-length. |
| • Narrow etched width. | • Wide propped width. |
| • Corrosion. | • Proppant transport. |
| • Compatibility. | • Screen-out. |
| • Temperature sensitive. | • Wellbore clean-out. |
| • Spent acid. | • Proppant flow back. |
| • Higher cost for fluid. | • Lower cost for fluid. |

## 14.2 Candidate Selection.

All carbonate formations can be candidates for Fracture Acidizing treatments. However, poorly performing wells due to low reservoir permeability and/or wells with restriction due to damage near the wellbore are more suitable as acid fracturing candidates.

Factors affecting well's productivity are:

1. Low reservoir permeability.
2. Damage in near-wellbore region.
3. Inefficient production equipment.

Well's productivity can be evaluated by:

1. Offset well comparison.
2. Production history curves.
3. Pressure transient analyses (buildup, draw-down, etc.).
4. Producing well system analysis.
5. List of damage indicators (well's report).

## 14.3 Acid-Fracturing Design Concepts.

In low to moderate-temperature wells, acid fluid-loss control may be the most important consideration. In high temperature wells, effective acid penetration distance often is limited by rapid spending, and retarded acid should be considered. In soft formation, such as chalks, the treatment should be designed specifically to maximise fracture conductivity.

As the acid flows along the fracture, portions of the fracture faces are dissolved. Since flowing acid tends to etch in a non-uniform manner to create conductive channels which usually remain open when the pumping pressure is released and the fracture closes. The effectiveness of the acid fracturing treatment is largely determined by the length of the etched fracture which is controlled by the volume of the acid used, acid reaction rate, and the acid fluid loss from the fracture into the formation. When designing an acid fracturing treatment, all factors affecting the success of the treatment must be considered:

- Pre-treatment formation evaluation.
- Production system analysis.
- Rock mechanics and fracture geometry.
- Rock solubility (reservoir temperature).
- Acid penetration.
- Acid and additives.
- Lab tests.

The following goals are expected after an acid fracturing treatment:

- The fracture propagated across the pay zone.
- The acid dissolved a large amount of reservoir rock.
- The acid etched the fracture faces unevenly to create channels with sufficient etched length and width that contained high conductivity after the fracture closed.
- Rapid and complete recovery of the treating fluids.
- Large fold of increase at a reasonable cost

## 14.4 Acid Fracturing Design Considerations.

### 14.4.1 Pre-treatment Formation Evaluation

a. Geologic considerations.

- Lithology: Carbonate (limestone, dolomite).
- Drainage area

  $x_f/r_e$ ratio.
  Fault patterns.

- Well logs.

  Porosity.
  Net pay.
  Water saturation.
  Mechanical properties. (Young's modulus, Poisson's ratio).
  Fracture height (temperature logs).

- Core analysis.

  - Conventional core analysis.

    Porosity.
    Permeability (5 to 100 folds high).
    Compatibility with stimulation fluids.

  - Special core analysis (in-situ).

    Permeability.
    Porosity.
    Relative permeability.
    Capillary pressure.

  - Oriented coring.

Natural fractures direction.
In-situ stress in three directions.
Fracture azimuth.

b. Well testing considerations.

- In-situ reservoir permeability.
- Skin factor.
- Reservoir pressure.
- Reservoir temperature.
- Reservoir fluid properties.

### 14.4.2 Production system analysis.

- IPR (flow in reservoir).
- Pressure drop across completion.
- Pressure drop in production string.

### 14.4.3 Rock mechanics and Fracture Geometry

a. In-situ stress:

- Fracture extension pressure
- Closure pressure

b. Basic rock mechanics and properties:

- Young's modulus (E) ( 8 to 13 x $10^6$ psi for limestone and dolomite)
- Poisson's ratio ($\upsilon$) ( 0.15 to 0.27 for limestone and dolomite)

c. Fracture geometry:

- Fracture height:

  Upper and lower barriers (stress contrast)
  Pump rate.

- Fracture models:

  KGD.
  PKN.
  Radial.

- Fracture half-length:

  Injection rate.

Leak-off rate.
Fracture height and width.
Volume pumped ($).

- Fracture width:

  Formation hardness (Young's modulus).
  Fluid viscosity.

- Fracture azimuth

  Perpendicular to minimum compressive principal in-situ stress.

### 14.4.4 Rock Solubility

- Greater than 70%.
- Limestones, dolomites, chalks.
- No insoluble reaction by-products.

### 14.4.5 Acid Penetration.

- Acid injection rate.
- Leak-off rate (worm-holes).
- Acid concentration.
- Formation temperature.
- Fracture width.
- Reaction rate.
- Composition of the formation.
- Effect of viscous fingering.
- Cost $ (volume -up to a certain point).

**Figure 22: Acid Penetration Versus Injection Rate.**

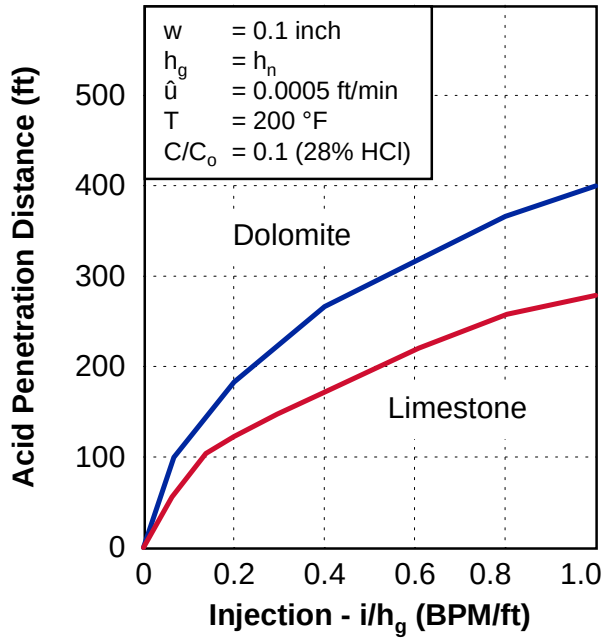
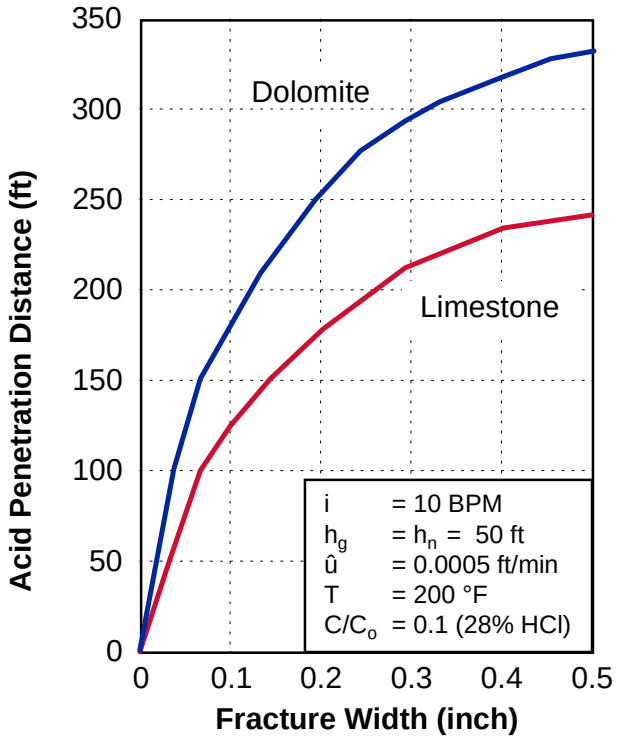



**Figure 23: Acid Penetration Versus Fracture Width.**



## 14.5 Fracture Geometry Considerations.

### 14.5.1 Fracture Azimuth.

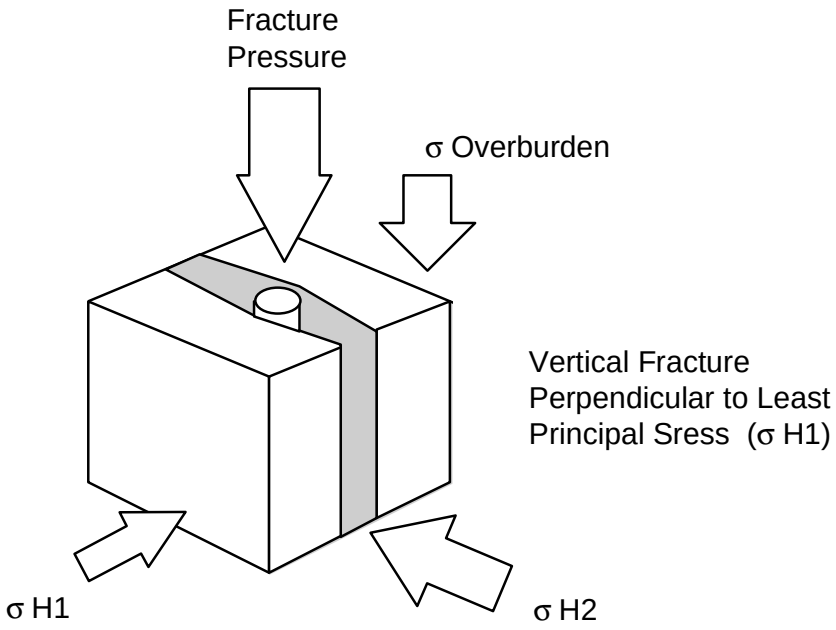
- Fracture will propagate perpendicular to the minimum, compressive, principal in-situ stress (take the path of least resistance and therefore opens up against the smallest stress). In-situ stress is the pressure that results from geologic changes such as folding and faulting that control the orientation of the fracture.

- The minimum stress in the earth's crust exerted in a horizontal direction, theoretically, would be equal to the effective overburden multiplied by the expression $\upsilon/(1-\upsilon)$, where $\upsilon$ is the Poisson's ratio of formation rock. The maximum horizontal confining stress would be equal to the effective overburden, which is true vertical depth (TVD) multiplied by the fracturing pressure gradient. (Effective overburden is defined as the acting or net-bearing pressure per unit area at any given depth.)

- In shallow wells (TVD < 1500'), the least principal stress is the overburden pressure therefore 'horizontal' fracture will be created.

- In deeper wells (TVD > 3000'), the least principal stress is one of the horizontal stress hence 'vertical' fracture will be created.

**Figure 24: Fracture Azimuth**



### 14.5.2 Fracture Length.

- Fracture half-length will be governed by fracture height for a given volume (fracture half-length ($x_f$) decreases as fracture height ($H_g$) increases).

- There exists an optimum fracture half-length for a given set of reservoir characteristics and conditions (permeability, thickness, pressure, etc.)

- Net pressure increases as $x_f$ increases. Barriers will be broken down if $x_f$ reaches a length where net pressure exceeds barriers' strength, hence $x_f$ will be limited.

- Length alone cannot indicate fracture effectiveness, fracture conductivity and reservoir permeability must be taken into consideration.

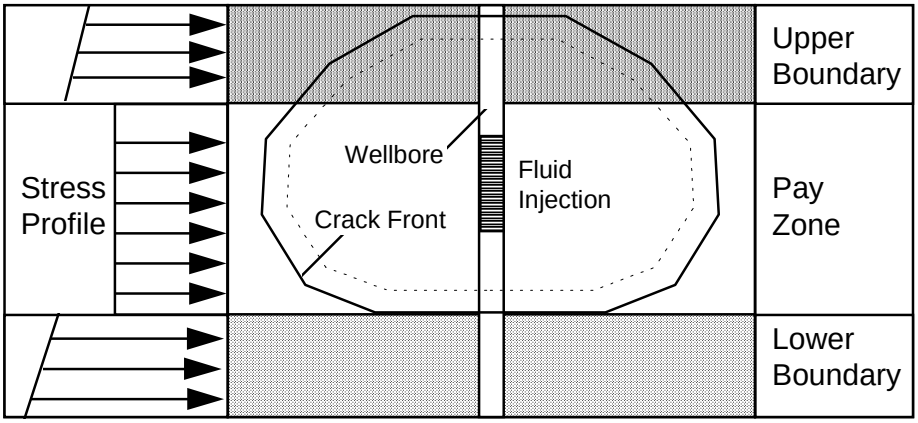
### 14.5.3 Fracture Width.

- Formation hardness (Young's modulus)
- Fracturing fluid viscosity (leak off coefficient)
- Volume
- Pump rate

### 14.5.4 Fracture Placement and Height.

- Must be initiated in proper zone (good cement job, correct perforations).
- Will propagate uniformly in uniform-stress formation.
- Change in fracture gradient (vertical stress, Poisson's ratio, rock type, etc.) will affect fracture growth and propagation.
- Fracturing pressure can indicate type of propagation and growth as it occurs.
- Temperature log is usually used to estimated fracture height.

**Figure 25: Fracture Placement and Height.**




## 14.6 Fracture Propagation Models

### 14.6.1 Two Dimensional (2-D) Models

Assuming definite upper and lower barriers:

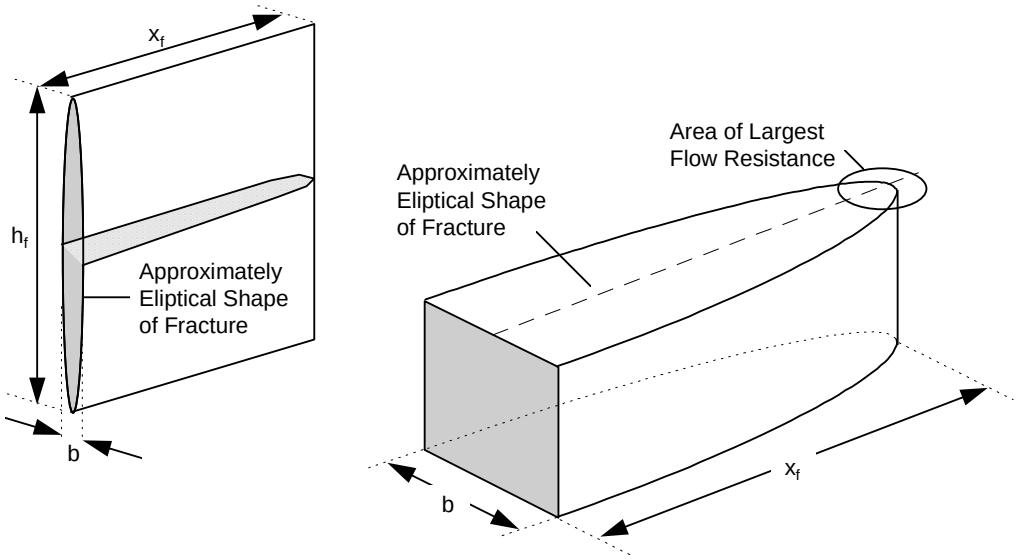
- KGD/GDK (Khristianovitch and Zheltov/; Geertsman and DeKlerk).

  Slippage at boundaries.
  Short and wide fracture.
  Net pressure decreases with volume (time).

- PKN (Perkins and Kern; Nordgren).

  No slippage at the boundaries.
  Narrow and longer fracture.
  Net pressure increases with volume (time).

**Figure 26: Fracture Propagation Profiles for PKN and GDK Models.**



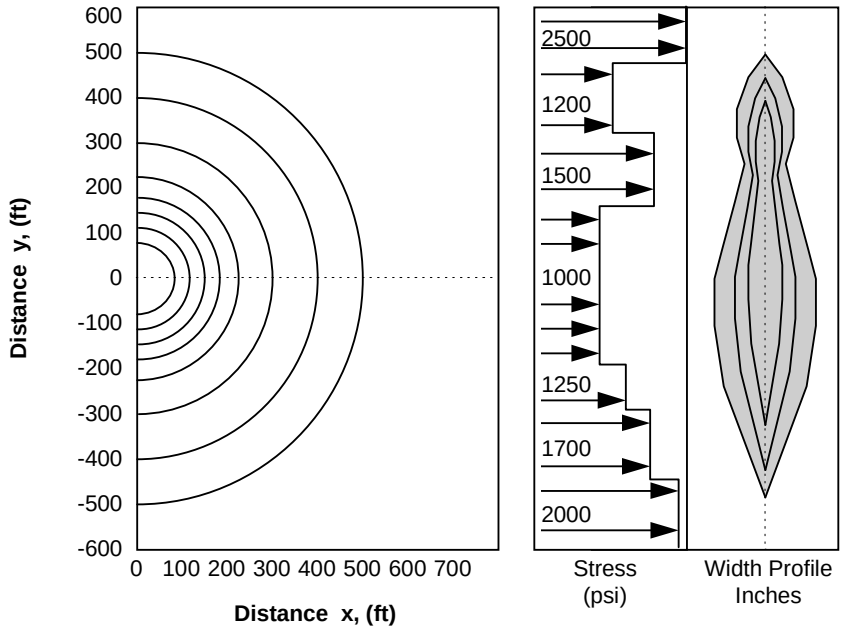

**Perkins & Kern** **Geertsma & DeKlerk**

### 14.6.2 Three Dimensional (3-D) Models.

Require information on vertical stresses along bore-hole:

- Radial or penny shape (for uniform stress formation).
- Fracture widths at wellbore depend on vertical stresses profiles.

**Figure 27: Fracture Propagation Profiles for Three Dimensional Models.**




## 14.7 Rock Solubility.

The only reservoir rocks soluble enough in acid to ensure large etched width are limestones, dolomites, and chalks. These rocks are mainly composed of calcite ($CaCO_3$) and dolomite ($CaMg[CO_3]_2$) minerals that are completely soluble in an excess of hydrochloric acid (HCl), formic acid (HCOOH) or acetic acid ($CH_3COOH$). These minerals are also soluble in hydrofluoric acid (HF) but would re-precipitate large amounts of potentially damaging calcium and/or magnesium fluorides. Hydrochloric acid has the largest dissolving power on carbonate formations. Formic and/or acetic (organic) acids are normally used at very high temperatures (above 300°F)

Very dirty carbonate rocks (with less than 70% solubility in HCl) and sandstones (even carbonate-cemented ones) are not candidate to acid fracturing. Etching would be impaired due to poor solubility. Insoluble materials released through the dissolution of the carbonate cement would plug the fracture and tremendously decrease its conductivity.

### 14.7.1 Acid Penetration.

The two major factors controlling the effectiveness of acid fracturing treatments are the etched fracture length and its conductivity. The effective fracture length is controlled by the acid fluid-loss characteristics, the acid reaction rate, and by acid flow rate in the fracture (which is a function of the pumping rate). Ultimately, the maximum acid penetration distance is limited by either fluid loss or acid spending. The acid reaction

rate usually depends on the rate of acid transfer to the wall of the fracture and not on the acid reaction kinetics. As a result, the flow rate of acid in the fracture and the fracture width are major factors in controlling acid spending.

Fracture conductivity also influences the effectiveness of the treatment. To produce adequate conductivity, the acid must react with fracture faces and dissolve a sufficient amount of the formation minerals. The manner in which the fracture faces are dissolved is as important as the amount of material removed. The fracture faces must be etched in a non-uniform manner to create conductive flow channels that remain open after closure of the fracture. Acid etching generally produces good conductivity as a result of selective acid attack (resulting from formation heterogeneity) and flow-induced selective etching effects. The conductivity is difficult to predict. One method of prediction simply assumes that fracture width is equal to the fracture volume created by rock dissolution at various positions along the fracture. Also it is assumed that fracture does not close. From these assumption, the ideal conductivity can be estimated by:

$$w\,k_f\,(max) = 7.8 \times 10^{12} \left(\frac{w_a}{12}\right)^3 \qquad (1)$$

where:

$w_a$ = etched width, inch
$w\,k_f$ = fracture conductivity, md-ft

This method gives overly optimistic estimates of fracture conductivity because it neglects the effect of fracture closure. Laboratory measurements of acid etched fracture conductivity have been attempted. However, these test results are generally not very reproducible and the measured conductivity are not representative of actual treating conditions because of small size of the sample used.

The fracture conductivity after an acid fracturing treatment is affected by:

- Closure stress.
- Rock embedment strength (formation hardness).
- Etched patterns (peaks and valleys of uneven fracture faces).

Ideally, the fracture conductivity after an acid fracturing treatment should be very high and yield an infinite 'Dimensionless Fracture Conductivity ($C_{fD}$)'. Theoretically, a $C_{fD} \geq 500$ is considered as Infinite Conductivity, however in practice, a $C_{fD} \geq 100$ is very difficult to obtain and therefore can be considered as infinite conductivity.

Dimensionless fracture conductivity also takes reservoir permeability into consideration in addition to fracture characteristics, and it is defined as:

$$C_{fD} = \frac{w\,k_f}{k\,x_f} \qquad (2)$$

where:

| | | |
|---|---|---|
| w | = | etched width, ft |
| $k_f$ | = | fracture permeability, md |
| k | = | formation permeability, md |
| $x_f$ | = | etched fracture half-length, ft |

## 15. Acid Systems and Additives for Fracturing.

Variables influence acid penetration before becoming spent include the volume acid used, fluid-loss control, acid concentration, injection rate, formation temperature, fracture width, and the composition of the formation.

### 15.1 Materials and Techniques for Acid Fluid-Loss Control

Controlling of fluid loss during acid fracturing of carbonate formations presents problems unique to reactive fluids. Fluid-loss additives and gelling agents normally used in non-reactive fracturing fluids are seldom stable in acid and are therefore ineffective due to rapid degradation. This has led to the development of special acid-stable additives required for acid fracturing treatments.

In addition to the problem of degradation, as acid flows across the faces of carbonate fracture, it constantly erodes the fracture surfaces, making it difficult for wall-building fluids to form an effective filter cake.

Acid tends to selectively enlarge certain large pores and hairline fractures, which results in "worm-holes" and channels perpendicular to the fracture faces. This further complicates the problem of leakoff and causes the rate of acid fluid loss to increase with time. Consequently, excessive fluid loss is generally considered to be the controlling factor that limits fracture growth and fracture extension when fracturing low to moderate-temperature carbonate formations.

Laboratory studies have shown that most acid fluid loss occurs from the worm-holes rather than uniformly into the face of the core. Nierode and Kruk (1973) suggested that acid fracturing fluids require much higher concentrations of fluid-loss additive for effective fluid-loss control than do non-reactive fluids. They also concluded that the only effective additive is a product composed of a mixture of oil-soluble resins. Oil-soluble resins eliminate the possibility of conductivity impairment (in oil wells or gas-condensate wells) when compared to 100-mesh sand in the fracture. However, acid fluid-loss additives have not been used extensively because of performance limitations and high cost.

#### 15.1.1 Viscous Pads.

One of the technique most commonly used for fluid-loss control involves the use of a viscous pad preceding the acid. The pad is used to initiate the wide fracture and to deposit a filter cake which will act as a barrier to fluid leakoff.

Low-viscosity linear gel pre-pads and high-viscosity cross-linked gel pads will also increase fracture width, which improves acid penetration and fracture conductivity. Multiple stages of a viscous pad, alternating with acid stages, will further improve acid fluid-loss (to the worm-holes) control, and therefore, the efficiency of the treatment is improved. This technique is widely used in acid fracturing treatments.

### 15.1.2 Foamed Fluids.

The use of foamed acid is one of the most effective methods for controlling acid fluid loss. Fluid-loss control is further enhanced by the use of a viscous pad preceding the foamed acid. However, foaming the acid does reduce the effective amount of acid available for etching since there is less acid present per unit volume of fluid injected. Therefore, 28% HCl should be used in preparing the foamed acid to maximise the amount of acid available for fracture etching. The primary advantages of foamed acid are its low fluid-loss and improved cleanup characteristics.

## 15.2 Materials and Techniques for Acid Spending Control.

Another major factor limiting penetration of live acid along fractures in carbonate formations is the spending of the acid. The acid reacts constantly with fracture surfaces and decreases in strength during its travel down the fracture. Once acid strength falls below about 10% of the original concentration, it is no longer capable of providing sufficient etching for acceptable fracture conductivity.

Higher acid concentrations increase penetration distance due to the greater amount of available acid. The more concentrated acid has a higher viscosity and generates more reaction products during spending, and both factors act to reduce the reaction rate.

### 15.2.1 Viscous Fluids.

Fracture width also has a significant influence on penetration distance. An increase in width results in an increase in acid penetration distance in both limestone and dolomite. This demonstrates the importance of using a viscous pad fluid preceding acid injection or the use of viscous acid, such as gelled acid or crosslinked acid. High-viscosity cross-linked gels are more widely preferred as pad fluids than low-viscosity linear gels since they have the advantage of creating wider fractures.

Temperature accelerates the reaction of acid on carbonate, an increase in temperature decreases acid penetration. Acid penetration distance in limestone is relatively less sensitive to temperature compared to that in dolomite. Pre-pads and/or pad fluids that precede an acid injection treatment will cool the tubular goods, which reduces corrosion, and cool the fracture, which reduces acid reaction rate and enhances live acid penetration.

At temperatures above 200 °F (93 °C), certain acrylamide-base copolymers, of a type commonly used to thicken acid, can be used in preparing pad fluids since they have good acid and temperature stability. The presence of a high-viscosity pad in the fracture promotes viscous fingering of the acid, which decreases the reactive surface area to which the acid is exposed. This fingering also tends to increase the effective conductivity of the etched fracture.

### 15.2.2 Chemical Retarders.

Retarders such as alkyl sulfonates, alkyl phosphonates, or alkyl amines reduce acid reaction rates by forming a hydrophobic film on the carbonate surfaces. This films act as a barrier which inhibits acid contact with the formation face and thus slows the acid reaction with the formation. Some retarders slow the reaction rate by blanketing carbonate surfaces with a thin layer of carbon dioxide foam which can be a stabilised by the presence of foaming agents.

### 15.2.3 Organic Acids.

Acetic and formic acids are sometimes used as retarded acids since they react at a much slower rate than hydrochloric acid at high temperatures. Their cost per unit dissolving power is higher than HCl, however, they are less corrosive, and therefore, can be inhibited at high temperatures for long periods of time. Inhibited acetic acid does not attack chrome plating, and small amount of formic acid in HCl may serve as inhibitor aid and reduce HCl acid corrosion.

## 15.3 Materials and Techniques for Improved Fracture Conductivity.

For an acid fracturing treatment to be effective, the wall of an acidized fracture must be etched sufficiently that conductive channels remain after the treatment. If the fracture faces are etched uniformly, the conductivity after the fracture closure is very low. Fortunately, several factors promote uneven etching of the fracture faces, such as mineral composition. Acid reacts with different minerals at different rates resulting in non-uniform etching.

The rate of acid reaction is also greatly affected by the acid flow velocity. Faster reaction rate at high flow rate results in the erosion of the fracture faces in areas of more rapid acid flow and creates erosion patterns. Once these channels develop, the acid tends to flow selectively along a few of the larger channels and most of the fracture faces remain relatively un-etched. This not only promotes increased fracture conductivity, but also increases live acid penetration.

Rock strength and closure stress are important factors affecting ultimate fracture conductivity. Crushing of fracture faces can result in loss of conductivity if the rock is too soft or closure stress is too high. Soft chalk formations are very prone to this problem.

The injection of a viscous pad fluid ahead of the acid is the most commonly used technique to maximise fracture conductivity. The presence of higher viscosity pad fluid promotes viscous fingering of the thinner acid which follows. This selective acid flow increases penetration distance and tends to create deep channels with good conductivity.

Propping agents also are used in acid fracturing treatments to obtain higher conductivity, especially for soft formations. The propping materials are injected near the end of the treatment to ensure good conductivity in the near-wellbore region.

## 16. Successful Acid Fracturing Stimulations.

Necessary Requirements

- Successful diversion.
- Open up natural fractures.
- Connect with the natural fracture system.
- Stimulate poor quality reservoirs.

### 16.1 Acid Fracturing Main Variables.

- Acid volume.
- Acid strength.
- Gelling of the acid
- Pump rate.
- Lead pad size.
- Number of stages used.

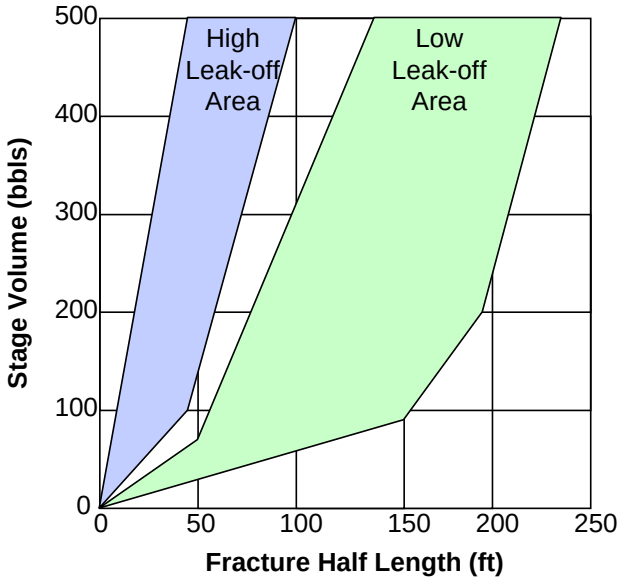
### 16.2 Acid Volume.

Based on experience in the North Sea.

- High Leak-Off Areas 200 Barrels per Stage.
- Low Leak-Off Areas 475 Barrels per Stage.

Increased fracture lengths can only achieved in areas with lower leak-off.

**Figure 28: Treatment Volumes (SPE 18225).**




### 16.3 Acid Strength Used in Acid Fracturing.

Both 15% and 28% HCl are used for different reasons:

28% HCl.

- Greater Penetration.
- Greater Conductivity.

15% HCl.

- Reduced dissolving power is not always important.
- Greater cost savings.

Low rock quality (low permeability and porosity) and poor natural fracture density require the use of 28% HCl.

### 16.4 Gelled Acid.

Previously Gelled acid systems have had limited use in places such as the North Sea whilst having several benefits:

- Reduced Leak-Off.
- Reduced Spending Rate.
- Reduced Friction Pressures.

Draw Backs

- Conventional acid gelling agents do not have breakers.
- Viscosity decreases with change in pH but leaves residual viscosity.
- Some data shows greater etched conductivity with non-gelled acid. This could be a function of test methodology i.e. reaction rate.

New Cross-Linked Systems (BJ Services XL Acid II).

- Breakers developed for crosslinked systems.
- Wider hydraulic fractures formed.
- Deeper penetration.

### 16.5 Pump Rates and Completions for Optimum Results.

Pump at greater than 30 Barrels per minute.

- Better Results. (140 Wells for Phillips Norway).

- Better Diversion.

Maximum treatable zone in one job:

- Minimize the number of perforated intervals (maximum 6 to 8).
- Minimum rate per perforation ( 0.10 to 0.15 Barrels/minute/perforation).
- Maximum number of discrete zones 6 to 8.
    - Maximum Perforation zone length 15 to 20 ft.
    - Maximum interzone spacing 40 to 60 ft.

## 16.6 Pad Volume and Characteristics.

Purpose of using a cross-linked pad:

- To induce a hydraulic fracture that will be etched by the acid.
- To produce a fracture of greater fracture width, with less leak-off than other fluids.
- To create radial fractures rather than linear fractures (acid).

A rule of thumb used for the volume of pre-pad required is 100 to 150% of acid treatment volume.

The breaking and clean of the pad fluid is usually accomplished by reaction with the acid or due to external breakers used with the fluid.

## 16.7 Acid Fracturing Diversion Techniques.

The use of ball sealers is the preferred method of diversion during acid fracturing.

- Positive and Negative buoyancy balls have been used.
- In general high density balls are preferred (1.1. sg or greater).
- High density balls fall into sump/rat hole.
- Small sizes preferred 5/8 inch balls for 0.375 inch perforations.

In horizontal or highly deviated wells:

- Buoyant balls required as no sump or rat hole.
- Low side perforations with zero degree phasing require use of buoyant balls.

Limited Entry Techniques:

- Where shot density is 2 shots per foot or less.
- Minimize net height of perforated interval.
- Benzoic acid flake in gelled pad can be used as diverter.

| Well | Diverter | Average Divert Pressure | Total Intervals | Intervals Treated | % Zone Stimulated |
|---|---|---|---|---|---|
| **A** | Benzoic | 113 | 6 | 4 | 67 |
| **B** | Benzoic | 463 | 5 | 3 | 60 |
| **C** | Balls | 860 | 6 | 6 | 100 |
| **D** | Balls | 965 | 3 | 3 | 100 |
| **E** | Balls | 1080 | 9 | 9 | 100 |
| **F** | Balls | 1730 | 9 | 7 | 78 |

### 16.8 Typical Fracture Treatments in the North Sea.

| | |
|---|---|
| Maximum total perforations | 150 to 180 ft. |
| Maximum discrete zones | 6 to 8. |
| Typical perforated interval (per zone) | 15 to 20 ft. |
| Fracture length with high natural fractures | 25 to 30 ft half length. |
| Fracture length with low natural fractures | 100 to 200 ft half length. |
| Acid volume | 300 gallons/ ft of perforations. |

**Average Treatments:**

| | |
|---|---|
| Gross Intervals | 480 ft |
| Net Interval | 88 ft |
| % Perforated | 18% |
| Number of zones | 7 |
| Pump rates BPM | 53 |
| Specific Rate | 0.23 bbl/d/perf |

## 17. Well Testing Prior to Acid Fracturing.

Prior to performing a fracture stimulation, a series of tests should be conducted to optimise the hydraulic fracture treatment design. Real time data recording and analysis should bed used. Where possible, water inflatable packers should be used when testing in open hole (less compressible than nitrogen). If possible down-hole pressure and temperature transducers should be included for more accurate measurement.

### 17.1 In Situ State of Stress Tests.

Used to determine which formations can contain a hydraulic fracture height growth. Isolate the selected zone in open hole and inject small volume of fluid (10 gallons to 2 barrels freshwater) at low rate (2 GPM to 0.5 BPM) until breakdown of formation occurs or a stabilised injection pressure is established. Record the bottom hole pressure during the test. Repeat the test several times to overcome near well-bore effects or until repeatable results are obtained. Carry out tests on each horizon in the open hole section to determine barriers to fracture height propagation.

### 17.2 Step Rate Tests.

Used to determine breakdown and fracture extension pressures. Fracture extension pressure is the stress that must be exerted on the rock to open a fracture and cause it to grow. Pressure during the test is measured and plotted against time. Analysis of the plot should show an inflection point in the rate of change of pressure which indicates the pressure at which fracture extension took place. Where two inflection points are seen at different pressures this indicates that the fracture has grown out of zone. These should be consistent in magnitude with minimum in situ stresses. Step rate tests can also be used to determine the magnitude of fracture tortuosity effects in the near well-bore, by differentiating between measured friction pressures and calculated perforation pressure drop, where no abrupt changes in net pressure and closure pressure can take place.

### 17.3 Pump In/Flow Back Tests.

Used to measure fracture closure pressure. Fracture closure pressure is the minimum horizontal stress in the rock less the fluid pressure in the fracture, and is one of the determinants of fracture conductivity. Fluid is pumped into the well at sufficient rate to cause fracture extension. The pumps are then shut down and the well allowed to flow at a constant rate, with the pressure being plotted as a function of time. An inflection point on this plot from concave upward to concave downward is interpreted as the fracture closure pressure. This test should be repeated several times to verify the closure pressure. Where two inflection points (closures) are seen this can indicate the presence of natural fractures or a horizontal component ("T" shaped).

## 17.4 Mini-Frac Treatments.

Used with actual fracturing fluid to measure fluid leak-off, fluid efficiency and gross vertical fracture height. The gross vertical fracture height determines the treatment size that must be pumped to achieve a given length and conductivity. Fracture fluid efficiency is the volume of the created fracture at the termination of pumping divided by the total volume of fluid pumped, and is a measure of fluid leak-off across the fracture face. Since fracture volume cannot be physically measured, fracture fluid efficiency and leak-off are derived from post fracturing pressure decay analysis.

Tests are usually conducted with using a volume ranging from 10% to 20% of the planned fluid volume without proppant at the planned injection rate. Radio active materials can be used to facilitate logging of the vertical fracture height.

## 18. Treatment Evaluations.

1. Monitor the pressure response when the acid contacts the formation and during injection.

   - The pump rate should be held constant throughout the job.
     If not, the pressure response record is useless.
   - The pressure should never increase when injecting the acid.
     If it does, the acid is damaging the formation.
   - If a pressure increase is seen when acid first arrives at the formation, it is probably plugging from solids that were present in the treating string. (A pipe pickling treatment should have been performed).
   - A gradual increase in treating pressure while acid is penetrating the formation, indicates precipitation of reaction by-products.
   - A slight increase in pressure should be seen when any diverter contacts the formation.
     If not, the diverter is probably ineffective.

2. Collect and analyse spent acid returns for:

   - pH
   - Iron content.
   - Presence of emulsions.
   - Amount, type and size of solids.
   - Presence of reaction.

3. Compare productivity improvement with productivity potential.

Real-time computer analysis of formation skin damage is now possible by using monitoring equipment to measure pressures and rates during the performance of the job. This information is then transferred to a computer for calculation of bottom hole pressure and various other parameters. With the computer program (FracRT) it is possible to optimise the size of an acid job (or stages) during the actual execution, as the skin damage is seen fall to a minimum. The program calculates and displays:

   a. Damage Ratio Value
   b. Paccaloni Style Injection Pressure vs. Injection Rate Plots.

Data collected during the job can be stored with the monitoring equipment (3600 or 3305 monitors) or on the computer and used for post job reporting and analysis.

## 19. Acid Jobs That Do Not Work.

Acid treatments which fail to stimulate production have usually been troubled by one or more of the following problems :

1. Using acid on formations which are inadequately perforated, or on sandstones which are not damaged.

2. Using the wrong type of acid to remove the damage.

3. Using dirty water in the preflush or overflush.

4. Lack of Hydrochloric Acid Preflush when using Hydrofluoric Acid with sandstones.

5. Inadequate mud acid volume, minimum volume should be 50 gallons per foot of pay.

6. Lack of immediate clean-up with mud acid, even with acid post-flush, allows deposition of precipitates.

7. Failure to clean the acid or water tanks.

8. Additive misuse or overuse.

9. Fracturing sandstones with acid (except with very small volume perforation breakdown treatments).

## 20. Quality Control.

1. Titrate the acid for strength. Refer to Table and Table for acceptable limits.

2. Check the service company's load sheet to make sure that all the additives are in the acid.

3. Agitate the acid on location prior to pumping to the well to ensure a uniform acid blend.

4. Determine the maximum surface treating pressure allowable to prevent fracturing of the formation.

5. Pressure test equipment to 5000 psi for 15 minutes

6. Maintain a constant injection rate during execution of the job. This will allow real time or post job analysis of pressure data to be performed.

7. Do not allow the use of transports and pumps that are used for anything other than acidizing services. This can lead to contamination of the acid.

8. Conduct a safety meeting on location to ensure that everyone knows what is to be done. Review all contingencies and safety procedures.

9. Take return acid samples each day until pH returns to that of the formation brine. Have samples analyses for the following :

    - pH.
    - Acid strength.
    - Surface tension.
    - Amount, size and type of solids.
    - Dissolved iron versus total iron.
    - Presence of emulsions and organic sludges.
    - Formation of precipitates.

**Table 20: Acceptable Range for HCl Acid Titration.**

| Acid Range Specified HCl (%) | Acid Range Acceptable HCl (%) |
|---|---|
| 7.5 | 6.0 to 9.0 |
| 15.0 | 13.5 to 17.0 |
| 20.0 | 18.5 to 22.0 |
| 28.0 | 26 to 30.0 |

**Table 21: Acceptable Range for HCl: HF Acid Titration.**

| Acid Range Specified HCl:HF (%) | Acid Range Acceptable HCl (%) | Acid Range Acceptable HF (%) |
|---|---|---|
| 7.5 :1.5 | 6.0 to 9.0 | 1.0 to 2.0 |
| 9.0 : 3.0 | 7.5 to 10.0 | 2.0 to 4.0 |
| 12.0 : 3.0 | 10.5 to 13.5 | 2.0 to 4.0 |

## 21. Method of Diluting Raw Acid.

To mix hydrochloric acid at a given strength, it is necessary to know the density of the raw acid in terms of Baumé (°Bé) or the Specific Gravity (s.g.). The first step in the mixing acid is to measure the density as follows:

1. Put a sample of the raw acid to be tested in a 250 cc cylinder and take the degrees Baumé (or specific gravity) reading with a hydrometer. Also take the temperature of the sample.

2. Correct the degrees Baumé or specific gravity to the standard temperature of 60° F (16° C) by using the correction factors listed in Table .

3. Convert the corrected degrees Baumé or specific gravity to percentage of HCl using Figure 29, page 148.

4. Use dilution charts (see Mixing Manual or Engineering Handbook) to determine how much raw acid is required to mix 1000 gallons (litres) of acid at the desired strength. Alternatively the following equation can be used.

$$\text{Gallons of Strong Acid Per 1000 gallons Weak} = \frac{1000 \times (\text{s.g. Weak Acid}) \times (\% \text{ Strength Weak Acid})}{(\text{s.g. Strong Acid}) \times (\% \text{ Strength Strong Acid})}$$

$$\text{Litres of Strong Acid Per 1000 Litres Weak} = \frac{1000 \times (\text{s.g. Weak Acid}) \times (\% \text{ Strength Weak Acid})}{(\text{s.g. Strong Acid}) \times (\% \text{ Strength Strong Acid})}$$

$$\text{Where °Bé} = 145 - \frac{145}{\text{s.g.}} \quad \text{or} \quad \text{s.g.} = \frac{145}{145 - \text{°Bé}}$$

To use Table to correct the degrees Baumé (Bé) or specific gravity to the standard temperature of 60° F (15° C), choose the °Bé or specific gravity reading closest to that of the reading measured with the hydrometer.

- If the acid temperature is above 60° F (15° C), add the correction value shown for every 1.0° F above 60 °F.

- If the acid temperature is below 60° F (15° C), subtract the correction value shown for every 1.0° F below 60 °F.

**Table 22: Temperature Corrections For HCl Hydrometer Readings.**

| Bé | Correction Factor (Bé) For Each °F | Specific Gravity | Correction Factor (s.g.) For Each °F |
|---|---|---|---|
| 2 | 0.01 | 1.014 | 0.0001 |
| 4 | 0.02 | 1.028 | 0.0001 |
| 6 | 0.02 | 1.043 | 0.0002 |
| 8 | 0.02 | 1.058 | 0.0002 |
| 10 | 0.03 | 1.074 | 0.0002 |
| 12 | 0.03 | 1.090 | 0.0002 |
| 14 | 0.03 | 1.107 | 0.0003 |
| 16 | 0.03 | 1.124 | 0.0003 |
| 18 | 0.04 | 1.142 | 0.0003 |
| 20 | 0.04 | 1.160 | 0.0003 |
| 22 | 0.04 | 1.179 | 0.0004 |
| 24 | 0.04 | 1.198 | 0.0004 |

Example.

| | | |
|---|---|---|
| Acid sample Hydrometer reading | = | 20.4 ° Bé |
| Acid Sample Temperature | = | 45 ° F |
| Correction Factor for 20 Bé | = | 0.04 per 1.0 °F |
| Temperature Difference from 60° F | = | 60 - 45 |
| | = | 15 ° F |
| Temperature correction | = | 0.04 x 15 |
| | = | 0.8 ° Bé |
| Temperature is below 60° F (subtract) | = | 20.4 - 0.8 |
| Corrected °Bé at 60° F | = | 19.6 ° Bé |
| Acid Strength (From Figure 29, page 148) | = | 30.6 % |
| Specific Gravity | = | 145 / (145-19.6) |
| | = | 1.156 s.g. |
| Required Acid Strength | = | 15 % HCl |
| Specific Gravity (From Figure 29, page 148) | = | 1.075 |

| | | |
|---|---|---|
| Raw acid required to mix 1000 gallons of 15% acid | = | $\frac{1000 \times 0.15 \times 1.075}{0.306 \times 1.156}$ |
| | = | $\frac{161.25}{0.3537}$ |
| Gallons of Raw acid required (at 19.6° Bé) | = | 455.9 gallons |
| Gallons of water required | = | 1000 - 455.9 |
| | = | 544.1 gallons |

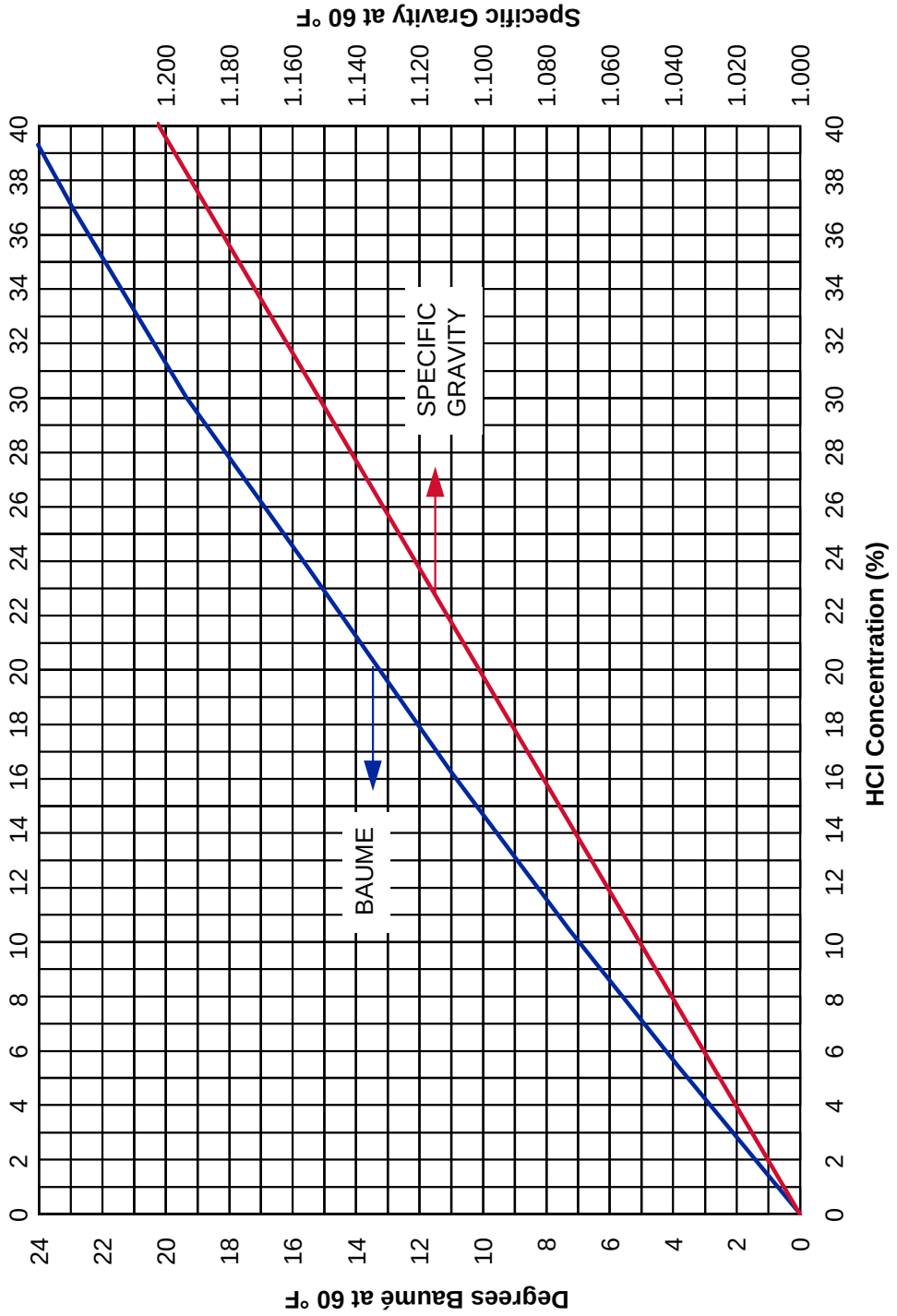
Note that when obtaining the volume of water required for proper dilution of the raw acid, that additives such as corrosion inhibitors, NE-Additives etc. are considered part of the dilution water requirement. Therefore, all additive volume must be subtracted from the volume of dilution water.

| | | |
|---|---|---|
| Corrosion Inhibitor (2.0 gallons/1000 gallons) | = | 2.0 gallons CI-Additive |
| NE-Additive (Non-emulsifier) 0.6% | = | 1000 x 0.006 |
| | = | 6.0 gallons |
| Total Additives | = | 6.0 + 2.0 |
| | = | 8.0 gallons |
| Water required | = | 544.1 - 8.0 |
| | = | 536.1 gallons |
| Final Mixing Requirements for 1000 gallons | = | 536.1 gallons Water |
| | = | 2.0 gallons CI-Additive |
| | = | 6.0 gallons NE-Additive |
| | = | 455.9 gallons Raw Acid |

If the volume of acid required for a job, or the mixing tank is greater or less than 1000 gallons a simple factor can be calculated to convert the required volumes. For example if the required volume was 750 gallons:

| | | | |
|---|---|---|---|
| Volume factor | | = | 750 ÷ 1000 |
| | | = | 0.75 |
| New Mixing requirements: | | | |
| Water | (0.75 x 536.1) | = | 402.1 gallons |
| CI-Additive | (0.75 x 2.0) | = | 1.5 gallons |
| NE-Additive | (0.75 x 6.0) | = | 4.5 gallons |
| Raw Acid | (0.75 x 455.9) | = | 341.9 gallons |
| Total | | = | 750.0 gallons |

**Figure 29: Density of Hydrochloric Acid Versus Percentage Composition**.




## 21.1 Acid Strength Determination by Titration.

The method of specific gravity or degrees Baumé measurements for determining acid strength is subject to error. Only the total amount of dissolved solids is being

measured. If an acid solution contains salt, the density of the solution will indicate a higher acid strength because the total amount of dissolved solids has been increased by sodium chloride dissolved in the solution. Therefore another method for determining the strength of acid solutions is recommended. The best, most common method of determining acid strength is a simple acid-base titration. This method can be used in the laboratory or in the field. For mixtures of HCl:HF acid, titration methods can also be used.

To determine acid strength by titration, the following equipment and reagents in the field titration kit are used:

- Syringe (1.0 ml and 5.0 ml).
- Glass Beaker (150 ml).
- Glass Stirring Rods (if available, use in step 2 instead of swirling).
- Distilled Water.
- 2.0 N Sodium Hydroxide (NaOH) solution.
- Phenolphthalein Indicator (Dropper Bottle).

The Procedure for determining the strength of HCl by titration is as follows:

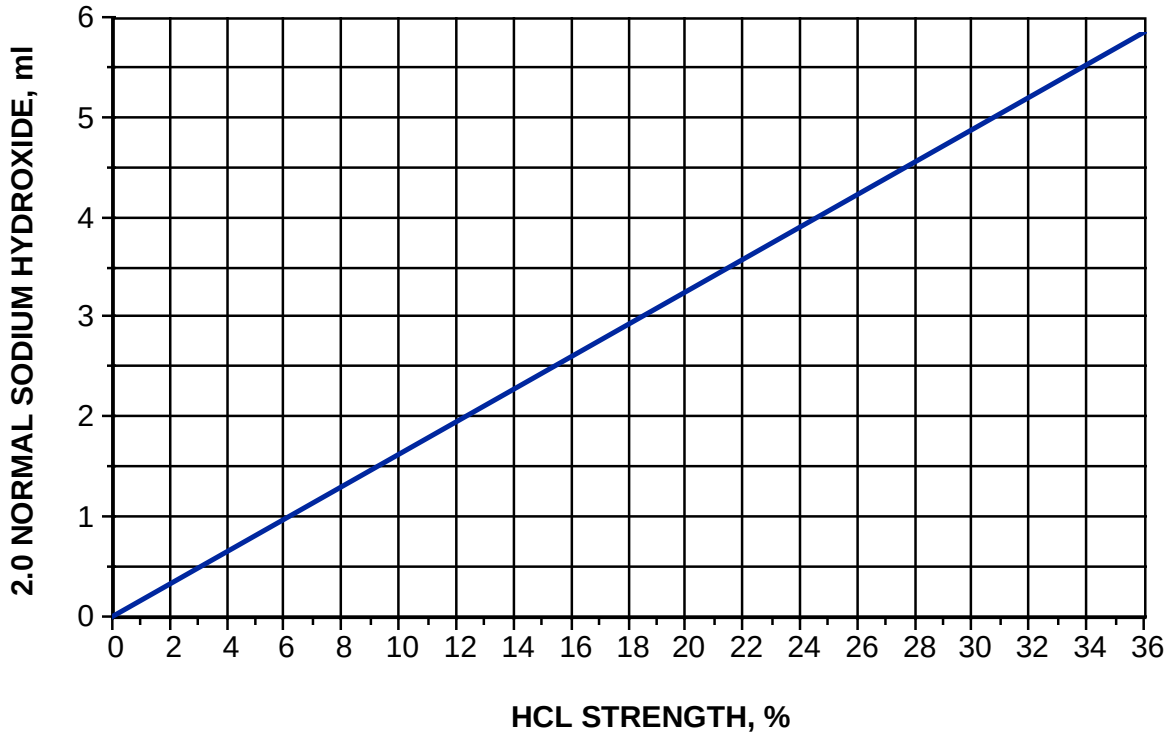
1. Place 1 millilitre of acid to be tested into a 150 millilitre Beaker. Dilute with distilled water to about 50 millilitres, and add two drops of Phenolphthalein indicator to the acid sample.

2. Using a 1.0 millilitre or a 5.0 millilitre syringe, add the 2.0 Normal sodium hydroxide drop-wise, whilst swirling the acid sample, until the acid turns pink. Record the number of millilitres of 2.0 normal sodium hydroxide used.

3. Determine the percentage of HCl in the acid from Figure 19.

This procedure gives the approximate percentage of HCl (±1.0%) and should be used as a field test only. For laboratory tests a 5.0 ml sample of acid should be used and a burette for measuring the 2.0 Normal sodium hydroxide.

**Figure 30: Determination of HCl Strength by Titration with Sodium Hydroxide.**




## 21.2 Loading and Mixing HCl Acid.

When preparing for an acid job, it must be ensured that the acid should be uniform throughout the tank. The raw acid, dilution water, and all additives must be thoroughly mixed together. The best loading method is as follows:

1. Load the volume of water (freshwater whenever possible) less the volume of additives needed.

   **Note :** Water should always be added first to prevent excessive heat being evolved and causing an explosion that can occur when water is added to raw acid.

2. Add the required concentration of inhibitor and NE-Additives separately. Do not mix any inhibitor or NE-Additives together or combine any NE-Additives in the same container. Chemical reactions can occur, and emulsion tests for proper additives would become useless. Always add each additive separately.

3. Add the volume of raw stock acid required to the volume of water and additives already in the tank. Keep the end of acid loading hose above the fluid level in the acid tank to aid in mixing the water, additives and acid.

4. When the required volume of liquid is placed in the tank additional mixing is necessary by one of the following methods:

   - Circulate the acid with a pump
   - Mix the acid with a paddle or auger (Where available).
   - Mix the acid by bubbling air for 10 to 15 minutes. This should not be used where other methods are available. Oxygen may become dissolved in the acid and create problems of corrosion in the well.

Agitation during transportation (where acid is premixed in transportation tanks) cannot be relied upon for properly mixing the treating solution.

### 21.3 Loading and Mixing HCl:HF Acid.

In sandstone stimulation, HF is normally used in combination with HCl. Mixtures of the two acids may be prepared by dilution mixtures of the concentrated acids with water or more commonly by the addition of fluoride salts such as ammonium bifluoride with water and then raw stock acid. The fluoride salts dissolved in water release HF when mixed with HCl. Fresh water should always be used for mixing HCl:HF acid, and no field waters containing sulphate, calcium, sodium or potassium ion should be used.

HF is poisonous, alone or in mixtures with HCl it should be handled with extreme caution. Mixing proportions of HCl:HF at various strengths using ammonium bifluoride can be found in the Engineering Handbook or in the Mixing Manual. Table to Table  can also be used for this purpose.

**Note:** The concentration of HCl required for mixing is always higher than the final concentration desired as part of the HCl is consumed in changing the ammonium bifluoride to HF.

Mixing HCl:HF requires rapid agitation or circulation of the water to facilitate the dissolving of the ammonium bifluoride, and proper mixing of all acid ingredients.

The following procedure should be used when preparing HCl:HF.

1. Place the required volume of dilution water in the acid tank.

2. With agitation, add the remaining ingredients in the following order to allow complete mixing or dissolving of the additives: corrosion inhibitors, NE-Additives and ammonium bifluoride.

3. With agitation, add the required amount of raw acid and agitate until uniform.

**Table 23: Mixing Quantities for HCl:HF Final Concentration of HCl required = 7.5%**

| Final Strength of HF Required (%) | HCl Strength Required to Mix (%) | Dilute HCl Volume Gal/1000 gal (Litre/$m^3$) | 33% HCl Volume Gal/1000 gal (Litre/$m^3$) | Fresh Water Volume Gal/1000 gal (Litre/$m^3$) | Ammonium Bifluoride lbs/1000 gal | Ammonium Bifluoride Kg/$m^3$ |
|---|---|---|---|---|---|---|
| 1 | 8.5 | 985 | 227 | 758 | 123 | 14.7 |
| 2 | 9.6 | 972 | 254 | 718 | 249 | 29.8 |
| 3 | 10.7 | 960 | 281 | 679 | 376 | 45.1 |
| 4 | 11.8 | 948 | 308 | 640 | 506 | 60.6 |
| 5 | 13.0 | 935 | 337 | 598 | 637 | 76.3 |
| 6 | 14.2 | 922 | 365 | 557 | 770 | 92.3 |
| 7 | 15.4 | 908 | 392 | 516 | 904 | 108.3 |

**Table 24: Mixing Quantities for HCl:HF Final Concentration of HCl required = 10.0%**

| Final Strength of HF Required (%) | HCl Strength Required to Mix (%) | Dilute HCl Volume Gal/1000 gal (Litre/$m^3$) | 33% HCl Volume Gal/1000 gal (Litre/$m^3$) | Fresh Water Volume Gal/1000 gal (Litre/$m^3$) | Ammonium Bifluoride lbs/1000 gal | Ammonium Bifluoride Kg/$m^3$ |
|---|---|---|---|---|---|---|
| 1 | 11.1 | 985 | 300 | 684 | 125 | 15.0 |
| 2 | 12.2 | 972 | 327 | 645 | 252 | 30.2 |
| 3 | 13.3 | 959 | 354 | 605 | 381 | 45.7 |
| 4 | 14.5 | 947 | 383 | 564 | 511 | 61.2 |
| 5 | 15.7 | 934 | 411 | 523 | 644 | 77.2 |
| 6 | 16.9 | 920 | 439 | 481 | 779 | 93.4 |
| 7 | 18.2 | 907 | 468 | 439 | 914 | 109.5 |

**Table 15: Mixing Quantities for HCl:HF Final Concentration of HCl required = 11.0%**

| Final Strength of HF Required (%) | HCl Strength Required to Mix (%) | Dilute HCl Volume Gal/1000 gal (Litre/$m^3$) | 33% HCl Volume Gal/1000 gal (Litre/$m^3$) | Fresh Water Volume Gal/1000 gal (Litre/$m^3$) | Ammonium Bifluoride lbs/1000 gal | Ammonium Bifluoride Kg/$m^3$ |
|---|---|---|---|---|---|---|
| 1 | 12.1 | 984 | 328 | 656 | 125 | 15.0 |
| 2 | 13.2 | 972 | 356 | 616 | 253 | 30.3 |
| 3 | 14.3 | 959 | 382 | 577 | 383 | 45.9 |
| 4 | 15.5 | 946 | 411 | 535 | 514 | 61.6 |
| 5 | 16.7 | 933 | 439 | 494 | 647 | 77.5 |
| 6 | 18.0 | 920 | 470 | 450 | 782 | 93.7 |
| 7 | 19.3 | 906 | 499 | 407 | 918 | 110.0 |

**Table 16: Mixing Quantities for HCl:HF Final Concentration of HCl required = 12.0%**

| Final Strength of HF Required (%) | HCl Strength Required to Mix (%) | Dilute HCl Volume Gal/1000 gal (Litre/$m^3$) | 33% HCl Volume Gal/1000 gal (Litre/$m^3$) | Fresh Water Volume Gal/1000 gal (Litre/$m^3$) | Ammonium Bifluoride lbs/1000 gal | Ammonium Bifluoride Kg/$m^3$ |
|---|---|---|---|---|---|---|
| 1 | 13.1 | 984 | 357 | 627 | 126 | 15.1 |
| 2 | 14.2 | 971 | 384 | 587 | 254 | 30.4 |
| 3 | 15.4 | 959 | 414 | 545 | 384 | 46.0 |
| 4 | 16.6 | 946 | 442 | 504 | 516 | 61.8 |
| 5 | 17.8 | 933 | 470 | 463 | 650 | 77.9 |
| 6 | 19.1 | 919 | 500 | 419 | 785 | 94.1 |
| 7 | 20.4 | 906 | 530 | 376 | 922 | 110.5 |

**Table 17: Mixing Quantities for HCl:HF Final Concentration of HCl required = 13.0%**

| Final Strength of HF Required (%) | HCl Strength Required to Mix (%) | Dilute HCl Volume Gal/1000 gal (Litre/$m^3$) | 33% HCl Volume Gal/1000 gal (Litre/$m^3$) | Fresh Water Volume Gal/1000 gal (Litre/$m^3$) | Ammonium Bifluoride lbs/1000 gal | Ammonium Bifluoride Kg/$m^3$ |
|---|---|---|---|---|---|---|
| 1 | 14.1 | 984 | 386 | 598 | 127 | 15.2 |
| 2 | 15.3 | 971 | 416 | 555 | 255 | 30.6 |
| 3 | 16.4 | 958 | 442 | 516 | 386 | 46.3 |
| 4 | 17.6 | 945 | 471 | 474 | 518 | 62.1 |
| 5 | 18.9 | 932 | 501 | 431 | 652 | 78.1 |
| 6 | 20.2 | 919 | 532 | 387 | 788 | 94.4 |
| 7 | 21.5 | 905 | 561 | 344 | 927 | 111.1 |

**Table 18: Mixing Quantities for HCl:HF Final Concentration of HCl required = 14.0%**

| Final Strength of HF Required (%) | HCl Strength Required to Mix (%) | Dilute HCl Volume Gal/1000 gal (Litre/$m^3$) | 33% HCl Volume Gal/1000 gal (Litre/$m^3$) | Fresh Water Volume Gal/1000 gal (Litre/$m^3$) | Ammonium Bifluoride lbs/1000 gal | Ammonium Bifluoride Kg/$m^3$ |
|---|---|---|---|---|---|---|
| 1 | 15.1 | 983 | 415 | 568 | 127 | 15.2 |
| 2 | 16.3 | 971 | 445 | 526 | 256 | 30.7 |
| 3 | 17.5 | 958 | 474 | 484 | 388 | 46.5 |
| 4 | 18.7 | 945 | 503 | 442 | 521 | 62.4 |
| 5 | 20.0 | 932 | 533 | 399 | 656 | 78.6 |
| 6 | 21.3 | 918 | 563 | 355 | 792 | 94.9 |
| 7 | 22.6 | 905 | 592 | 313 | 931 | 111.6 |

**Table 19: Mixing Quantities for HCl:HF Final Concentration of HCl required = 15.0%**

| Final Strength of HF Required (%) | HCl Strength Required to Mix (%) | Dilute HCl Volume Gal/1000 gal (Litre/$m^3$) | 33% HCl Volume Gal/1000 gal (Litre/$m^3$) | Fresh Water Volume Gal/1000 gal (Litre/$m^3$) | Ammonium Bifluoride lbs/1000 gal | Ammonium Bifluoride Kg/$m^3$ |
|---|---|---|---|---|---|---|
| 1 | 16.1 | 983 | 445 | 538 | 128 | 15.3 |
| 2 | 17.3 | 971 | 475 | 496 | 257 | 30.8 |
| 3 | 18.5 | 958 | 504 | 454 | 390 | 46.7 |
| 4 | 19.8 | 945 | 535 | 410 | 523 | 62.7 |
| 5 | 21.1 | 931 | 565 | 366 | 658 | 78.9 |
| 6 | 22.4 | 918 | 595 | 323 | 796 | 95.4 |
| 7 | 23.7 | 904 | 623 | 281 | 935 | 112.1 |

**Table 30: Mixing Quantities for HCl:HF Final Concentration of HCl required = 16.0%**

| Final Strength of HF Required (%) | HCl Strength Required to Mix (%) | Dilute HCl Volume Gal/1000 gal (Litre/$m^3$) | 33% HCl Volume Gal/1000 gal (Litre/$m^3$) | Fresh Water Volume Gal/1000 gal (Litre/$m^3$) | Ammonium Bifluoride lbs/1000 gal | Ammonium Bifluoride Kg/$m^3$ |
|---|---|---|---|---|---|---|
| 1 | 17.2 | 983 | 478 | 505 | 128 | 15.3 |
| 2 | 18.3 | 970 | 504 | 466 | 259 | 31.0 |
| 3 | 19.6 | 957 | 536 | 421 | 392 | 47.0 |
| 4 | 20.8 | 944 | 564 | 380 | 525 | 62.9 |
| 5 | 22.1 | 931 | 594 | 337 | 662 | 79.3 |
| 6 | 23.5 | 917 | 626 | 291 | 799 | 95.8 |
| 7 | 24.9 | 903 | 658 | 245 | 939 | 112.5 |

## Index.